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Surface reactions with participation of oxides of molybdenum and tungsten: the influence of external factors

This work is a continuation of the article "Surface reactions with participation of oxides of molybdenum and tungsten", published in the previous issue of the journal. The influence of the electric field and the pressure of oxygen in the gas phase on the rate of surface reactions for the synthesis of molybdates of manganese and copper were investigated. It's found that for the synthesis reaction of molybdate of copper the nature of the dependency of the rate of synthesis and rate of surface reactions from the external parameters are the same, indicating the crucial contribution of surface diffusion to the reactive mass transfer. For the synthesis reaction of molybdate of manganese the dependences of the rate of synthesis and of rate of surface reactions by external parameters differ, indicating that for this reaction, surface diffusion isn't the main mechanism of mass transfer.

Introduction

In a number of experiments to study solid state reaction of synthesis of molybdates and tungstates it was observed that the reaction product is not only in the place of the direct contact of the briquettes of reagents (diffusant and substrate), but also outside it, on the free surface of the substrate briquette, fig. 1.

This phenomenon, as well as the results of experiments on the effect of substrate porosity on the rate of solid state reactions [1] prompted us to conduct a special study of the surface reaction diffu-sion (SRD), the results of which we published earlier in [2–4]. The reaction diffu-
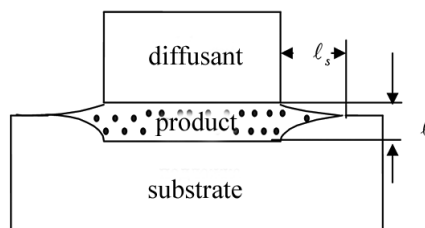

Fig. 1. The disposition layout of the briquettes of the starting materials and the layer of product

sion in the synthesis of molybdates and tungstates, as with many other complex oxides, includes bulk, grain boundary and surface mass transfer.

To explore the features of the mechanism of surface mass transfer and to assess its contribution to the reaction stream has been tasked to studying of the influence of external factors on the rate of surface reaction, characterized by the length of the surface layer ℓ_s, and on reaction rate in general, characterized by the thickness of layer of product in the place of contact of the briquettes reagents ℓ.

The experimental part

We used CuO, MoO_3, Mn_2O_3, (qualifying "h.p."). The samples for investigation were prepared in the form of briquettes by pressing and subsequent sintering. Sintering conditions of the samples are given in table 1.

Table 1.
Sintering conditions of the samples.

Compound	Temperature of sintering, °C	Time of sintering, hour
Mn_2O_3	900	24
CuO	950	18
MoO_3	600	3

When studying of SRD in the electric field the bars of the substrate with a height of 3–5 mm and tablets of diffusant with a diameter of 15 mm and a thickness of 1.5–2.0 mm were used. Surface of the reagents was carefully polished before experiments to remove surface contamination. The reaction couple, which is of constant thickness, with platinum electrodes were placed in a corundum cell, which, in turn, was placed in the furnace preheated to the required temperature, then a constant voltage from the power source is supplied into the system. The control for the development process was performed by the measurement of the length of the surface layer ℓ_s and the thickness of the layer of product ℓ in the place of contact the briquettes. The layout of the briquettes of the starting materials and of the layer of product in the study of SRD in an electric field are presented in fig. 2.

The diffusion anneals under reduced oxygen pressure were performed in the interval of $P_{o_2} = 1 \div 10^{-5}$ atm. The oxygen pressure in the system was setting by the electrochemical oxygen pump from stabilized Zirconia (ZrO_2 + 10 mol % Y_2O_3) and was controlling using an oxygen sensor made of the same material.

X-ray analysis of the reaction product was carried out on diffractometer DRF-2.0 by radiation $Co_{K\alpha}$. The survey was conducted at a speed of 2.0 °/min in the range of angles 2θ from 5 to 35 °.

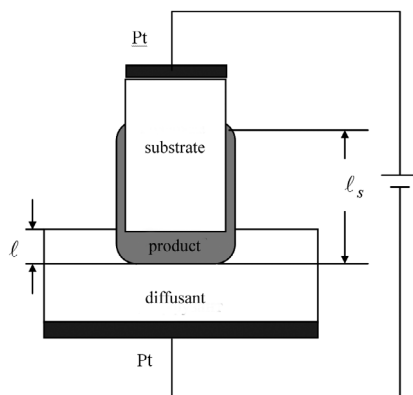Microscopic analysis of the surface and of chips of the briquettes after annealing was performed using microscope MBS-9

Fig. 2. The layout of the briquettes of the starting materials and of the layer of product in the study of SRD in an electric field (U = const).

with magnification in 16 to 56 times and optical microscope POLAM-112 in transmitted light at magnification of 300–420 times.

The measurement of the mass of briquettes before and after diffusion annealings was carried out on an analytical balance Sartorius – BL60S with an accuracy of 0.0001 g

The effective density of samples was determined by the volume and mass of samples and hydrostatic weighing. Its value ranged from 60 to 85 %. The morphology of the substrate and product, as well as their elemental composition was investigated using the electron microscope JSM-3 with a microanalyzer at magnification of 300 - 3000 times.

Results and discussion

The influence of an electric field.

The influence of the electric fields at SRD (ℓ_s) and the rate of solid-phase reactions in general (ℓ) for two systems CuO-MoO$_3$ и Mn$_2$O$_3$-MoO$_3$, in which the reactions occur:

$$2Mn_2O_3 + 4MoO_3 \rightarrow 4MnMoO_4 + O_2 \quad (1)$$
$$2CuO + MoO_3 \rightarrow Cu_2MoO_5 \quad (2)$$
$$(CuMoO_4)$$
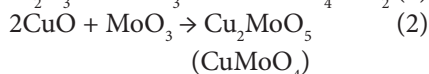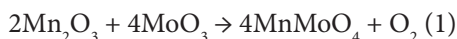
In brackets there is the minor product of the reaction.

The experiment was conducted at a temperature of 600 °C with potentiostatic conditions; the voltage on the reaction cell was varied from –400 to +400 V when the thickness of the assembly of briquettes was 5 mm.

For the positive direction of passing of the electric current it's adopted such direction when the briquette of MoO$_3$ is positively polarized, and the substrate ((CuO, Mn$_2$O$_3$) is negative: (–) substrate|MoO$_3$ (+), $U > 0$. The dependence of characteristics of the process velocity from the voltage is presented in fig. 3–4.

For the system CuO-MoO$_3$ was found that electric field significantly influences the rate of surface reaction and the overall rate of synthesis. The length of the surface layer depending on the voltage level and direction of transmission of the electric current varies from 90 to 1300 µm, and the thickness of the layer in the place of contact varies from 10 to 130 µm (fig. 3). Thus, the influence of an electric field in the range of values of $U = $ –400...+400 allows to change the value of 14 times and to change the value of 13 times. This shows that the intensity of influence of the electric field on the rate of surface reaction and reaction rate in general is about the same.

As can be seen from fig. 3, the nature of the effect of electric field on the rate of surface reaction and speed of interaction in the place of contact is similar. This indicates a similar mechanism of the SRD and interaction at the site of contact of the briquettes of the reagents. In place of
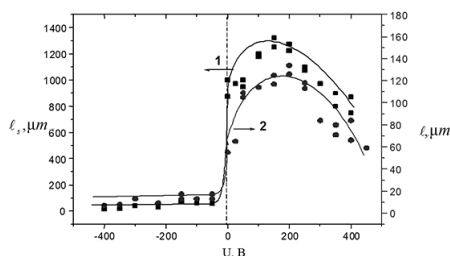

Fig. 3. The dependence of the length of the surface layer (1) and the thickness of the layer (2) in the place of contact of the briquettes reagents from the voltage on the cell of the CuO-MoO$_3$, $t = 600$ °C, $\tau = 3$ hours

the contact the mass transfer is carried out both by surface and by grain boundary and bulk diffusion. The same nature of the impact of electric field on the SRD and on the speed of interaction at the site of contact, it seems, may be an indication that surface diffusion is the main mode of mass transfer in this system.

The complex non-monotonic character of the dependences can be explained within the framework of the hypothesis about electroosmotic entrainment of MoO_3 by counterions of the double electric layer arising at the interfaces, along which there is a transfer diffusant. The essence of this hypothesis is described in detail in [1–2, 5].

For the system Mn_2O_3/MoO_3 the strong effect of electric field on the rate of surface reaction (ℓ_s) and reaction in general (ℓ) is also found, fig.4.

The length of the surface layer depending on the voltage level and direction of transmission of the electric current ranges from 1200 to 2000 μm, and the thickness of the layer in the place of contact ranges from 3 to 24 μm

Thus, the influence of the electric field in the range of values of $U = -300 ...+300$ V allows to change ℓ_s 1.7 times, and ℓ allows to change 8 times. This shows that the intensity of the influence of the electric field on the rate of surface reaction is much less than the rate of reaction in general.

The shape of curves $\ell_s, \ell = f(U)$ is also very different (fig. 4). In the field of values of voltage -80...+50V the nature of the influence of the electric field ℓ on and ℓ_s is opposite: an increase in the voltage increases the layer thickness at the site of contact of the reagents and decrease of the length of the surface layer. This shows the difference of the mechanism of mass transfer at the surface and at the site of contact. Apparently, in this system, the surface diffusion isn't the main transport stream, which presumably can be grain-boundary diffusion.

Influence of oxygen activity in the gas phase on the rate of surface reactions.

The layout of the briquettes of the reagents and reaction product in studies of the reaction diffusion at the different pressures of oxygen is presented in fig. 5.

In these series of experiments there was radial (two-dimensional) distribution of diffusant on the substrate surface.

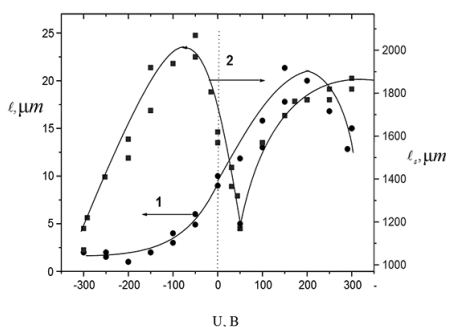To discuss the results of experimental values ℓ and ℓ_s the rate constants of

Fig. 4. The dependence of the thickness
of the layer at the site of contact of briquettes
of the reagents (1) and the length
of the surface layer(2) of the voltage on
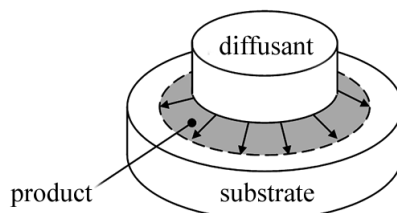the cell Mn_2O_3-MoO_3, t = 600 °C, τ = 3 hours

Fig. 5. The layout of the briquettes
of the reagents and reaction product

the interaction at the site of contact of the briquettes of reagents (K) were calculated by the equation $K = \ell^2/\tau$ and the rate constant of surface reaction (K_s) were calculated according to the equation $K = x\ell^3 + y\ell^3 + z\ell^3 / \tau$. This type of constant K_s is due to fact that for radial diffusion the growth of the surface layer is described the third-order polynomial as shown in our article published in the previous issue of the magazine:

$$x\ell_s + y\ell_s^2 + z\ell_s^3 = \Delta G\tau \qquad (3)$$

The dependences of the rate constants from p_{o_2} in logarithmic coordinates are presented on fig. 6.

For the system Mn_2O_3-MoO_3 values of $d\ell gK_s/d\ell gP_{O_2}$ and $d\ell gK/d\ell gP_{O_2}$ are respectively –1/6 and –1/4, and for the system CuO-MoO_3 are respectively –1/8 and –1/9

Thus, for both systems, the decrease of the oxygen pressure increases the speed of interaction, both on the surface and at the site of contact.

As was proved earlier in [1–2], the main mechanisms of mass transfer during the synthesis of molybdates are the surface and grain-boundary diffusion.
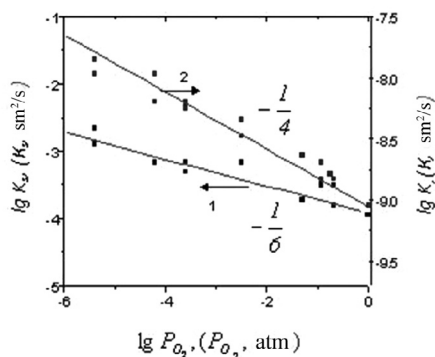
The speed of these reactions is proportional to the concentration of extended defects and, apparently, little depends on the concentration of point defects. About the veracity of this claim the following fact is evidenced. The diffusion coefficient of molybdenum in monocrystal $PbMoO_4$, determined by the method of radioactive indicators, increases with growth p_{o_2}: $D_{Mo} = K \cdot P_{o_2}^{+1/7}$ [6], which indicates the growth of point defects in molybdenum sublattice with growth p_{o_2}. At the same time, the reaction rate of the formation of $PbMoO_4$ decreases with increasing p_{o_2} [6].

The chemical nature and mechanism of formation of extended defects in complex oxides are poorly understood to date. Therefore, the quantitative interpretation of the dependence of the rate of surface reactions and reactions at the site of contact of the synthesis of molybdates is not possible to the present moment.

On a qualitative level the increase in the rate of surface interaction with decreasing p_{o_2} can be explained as follows. According to [7], in the lattice of complex oxides $MeMoO_4$, especially at the interfaces the defects of the type $O_{MoO_4}^x$ capable
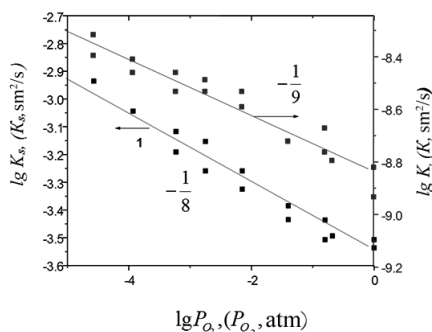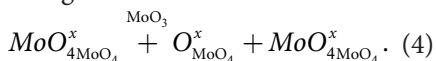

Fig. 6. The dependence of the constants K_s and K from the pressure of the oxygen in the gas phase in the system Mn_2O_3-MoO_3 (t = 600 °C, τ = 3 hours)

Fig. 7. The dependence of the constants K_s and K from the pressure of the oxygen in the gas phase in the system CuO-MoO_3 (t = 600 °C, τ = 3 hours)

of migration of the component Mo in the following manner can contain:

$$MoO_{4MoO_4}^x + \overset{MoO_3}{O_{MoO_4}^x} + MoO_{4MoO_4}^x. \quad (4)$$

The mobile form is triangular pyramid (MoO_3) which has properties that potentially facilitate the migration of Mo:

first, can rotate around the Mo-peaks due to the oxygen exchange with the vacant position,

secondly, a pyramidal center MoO_3 with a tricoordinated atom Mo can in principle change its shape by passing Mo through the center of the base of the pyramid, fig. 8 [7].

It is logical to assume that with increasing defect the concentration of the type $O_{MoO_4}^x$ will increase the rate of mass transfer of molybdenum oxide through the layer of reaction product and, consequently, the rate of reaction. Defects $O_{MoO_4}^x$ may form at the exit of MoO_3 from the crystal lattice $MeMoO_4$ into the gas phase on the reaction:

$$MeMoO_4 \Leftrightarrow MoO_3(\text{газ}) + Me_{Me}^x. \quad (5)$$
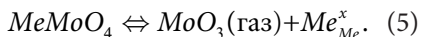
In order to evaluate the effect of reducing the partial pressure of oxygen at equilibrium (5) the following experiment was carried out. The pre-weighed briquettes of molybdenum oxide were annealed in an oxygen 10-5 atm) at ×atmosphere (p_{o_2} = 1 atm) and in the helium atmosphere (p_{o_2} = 3×10⁻⁵ atm) and at the°temperature of 600
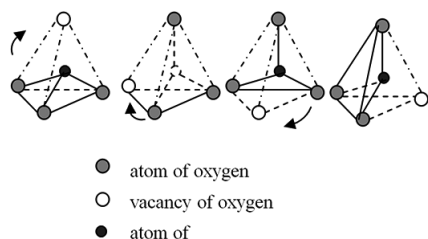

○ atom of oxygen
○ vacancy of oxygen
● atom of

Fig. 8. The inversion center of MoO_3 [7]

°C during 15 hours and the change in mass after annealing was determined. Since the briquettes have different weight and volume, the change in mass was resulted in the area of the entire surface of the briquettes. The results of the experiment are shown in table 2.

Table 2
The mass decrease of the MoO_3 briquettes, annealed in an atmosphere of oxygen and helium, t = 600 °C, τ = 15 hours.

p_{o_2}, atm	1 (oxygen)	3·10⁻⁵ (helium)
$\dfrac{\Delta m}{S} \cdot 100\ \%$, g/sm³	0,24%	0,39%

The results in table show that the mass decrease of the briquettes in an atmosphere of helium at about 1.6 times more than in the atmosphere of oxygen. Likely the increase of the volatility of molybdenum oxide at low oxygen pressure shifts the equilibrium (5) in the direction of the products, i.e. increasing the concentration of defects $O_{MoO_4}^x$. This, in turn, leads to an increase in the rate of mass transfer of molybdenum oxide through the layer of reaction product and to increase the of the reaction rate, as observed experimentally.

Assessing the results of impact pressure of oxygen in the gas phase on the reaction rate in the investigated systems, we also note that the proximity coefficients $d\ell g K_s / d\ell g P_{O_2}$ and $d\ell g K / d\ell g P_{O_2}$ for the system of $CuO\text{-}MoO_3$ may be an indication that surface diffusion is the main mode of mass transfer in this system.

The difference of these coefficients for the system $Mn_2O_3\text{-}MoO_3$, likely is due to the fact that surface diffusion is the main transport stream in the synthesis of $MnMoO_4$. These findings are in good agree-

ment with the conclusion made by us above, according to the data of the effects of electric fields on the reaction rate.

Study of the morphology of the substrate and reaction product by electron microscopy.

The morphology of the substrate and the reaction product was examined by electron microscopy to determine possible differences for the studied systems.

System CuO-MoO$_3$

Under the interaction of CuO and MoO$_3$ the formation of two individual chemical compounds CuMoO$_4$ and Cu$_2$MoO$_5$ may occur. The main product of the interaction is Cu$_2$MoO$_5$ and only after prolonged annealing (more than 30 hours) at the site of contact of the briquettes by means of XPA recorded trace amounts of the second phase - CuMoO$_4$ were recorded. Studies by electron microscopy gave the following information.

The grains of CuO substrate have the form of irregular polygons; the size 5.5–13 μm, fig. 9.

The grains of reaction product Cu$_2$MoO$_5$ have an elongated shape, their size varies from 2 to 5 microns in width and from 8 to 20 μm in length, fig. 10.

Thus, in this system the grains of the product and substrate are quite similar in size but differ shape.

System Mn$_2$O$_3$-MoO$_3$

The grains of the substrate Mn$_2$O$_3$ have a rounded shape, their average size is of 2.5 μm, fig. 11.

The grains of reaction product Mn-MoO$_4$ also have a rounded shape, but their average size (10 μm) was approximately 4 times larger than the grain size of the substrate, fig. 12.

Thus, the fundamental differences in the morphology of the grains of the product and the substrate (the form of grains, the ratio of the grain size of the substrate/product) are revealed for the two studied systems This fact indirectly indicates differences in the mechanism of the reaction diffusion in the investigated systems.

Conclusions

In terms of the results of this work we can draw the following conclusions:

1. It is established that the nature of the impact of electric field on the rate of surface interactions and reaction speed in general is the same for the synthesis
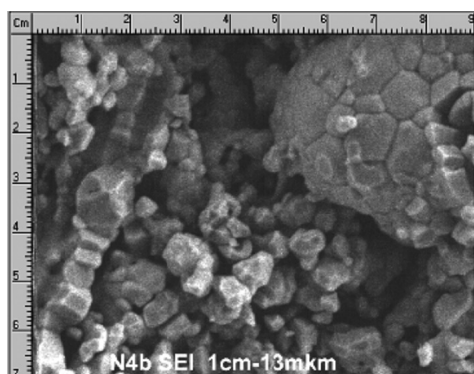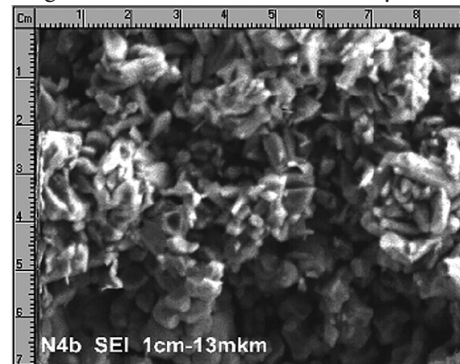

Fig. 9. The SEM image of the CuO substrate

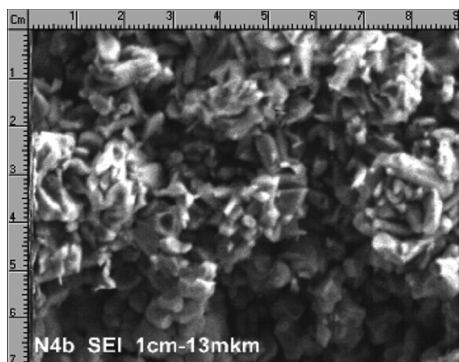Fig. 10. SEM image of product Cu$_2$MoO$_5$
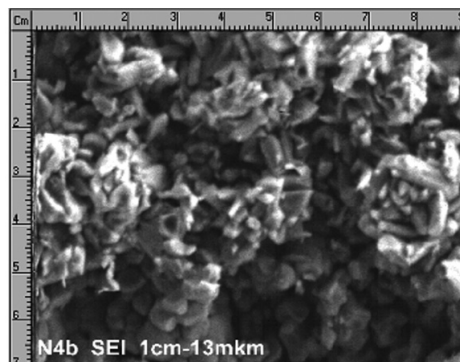
Fig. 11. SEM image of substrate Mn_2O_3

Fig. 12. SEM image of product $MnMoO_4$

of copper molybdate and is varied for the synthesis of manganese molybdate.

2. It is established that decreasing of oxygen pressure leads to increased speed of interaction both on the surface and in the region of contact of the reagents for the systems CuO/MoO_3 and Mn_2O_3/MoO_3, which may be associated with an increase in the concentration of defects of type $O_{MoO_4}^x$ under decreasing of oxygen pressure. The intensity of the impact on the speed of surface interactions and reaction speed in general is close for the syn-thesis of copper molybdate and differs for the synthesis of manganese molybdate.

3. By electron microscopy the mor-phology of the substrates and reaction product in the systems CuO/MoO_3 and Mn_2O_3/MoO_3 was researched. The differ-ences in the form of grains, and the ratio of the grain sizes of the product/substrate in the investigated systems were determined.

4. The educated guess was made about that the main traffic stream in the synthe-sis of copper molybdate is surface diffu-sion, in contrast to the synthesis of man-ganese molybdate.

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