ON THE POSSIBILITY OF THE REACTION (CuMoO4 + C), USING THE APPARENT ACTIVATION ENERGY METHOD

This article discusses the calculation of the apparent activation energy (CuMoO$_4$ + C) on the DTA (Differential Thermal Analysis) curve, to study and optimize the time-temperature synthesis mode, in particular, the activation energy. Activation energy allows us to investigate the elementary act of chemical interaction. Thus, we propose to use this method to calculate the interaction of Eact (CuMoO$_4$ + C) in the solid phase of hardening occurring during synthesis. These results allow us to trace how much energy is expended to start the reaction.

Key words: copper molybdate, carbon, DTA, the activation energy

INTRODUCTION

The most common method for producing molybdenum is oxidative roasting of molybdenum concentrates [1]. The resulting calcine contains molybdenum trioxide other compounds and impurities such as CuMoO$_4$. Trioxide is produced by the sublimation of cinders or hydrometallurgical method [1].

Oxidation of molybdenite in this method is carried out by its decomposition with nitric acid, oxidation with oxygen under pressure in an alkaline or acidic media followed by treatment with sodium hypochlorite solutions of the concentrate [1].

To obtain high purity molybdenum trioxide or molybdenum concentrates stubs chlorinated to produce condensate easily volatile (lVOZG = 160 °C) dioxide chloride molybdenum MoO$_2$Sl$_2$ [1].

THEORETICAL ANALYSIS

When processing molybdenum concentrates to extract commercial products such as copper and molybdenum oxide by pressure leaching, oxidative chlorination roasting and because of their complexity, require costly and time.

In this regard, obtaining copper and molybdenum oxide from the sample CuMoO$_4$ by reduction using carbon as a reducing agent for the first time is of undoubted interest.

To study and optimize the temperature-time mode of synthesis of various compounds with carbon, in this case CuMoO$_4$ + C requires knowledge of the kinetic pa-

rameters of the interaction of carbon flowing in the synthesis, in particular, the activation energy measured derivatograph.

Original equation to calculate the kinetic parameters of the reactions is the Arrhenius equation

$$K = A \cdot exp(-E_{act}/RT), \qquad (1)$$

where: E_{act} - activation energy, A - pre-exponential factor, which does not depend on the temperature in a small temperature range, R - gas constant, T - absolute temperature.

For the case of the expansion rate of the solids is expressed by the equation

$$V = k (1 - a)^n, \qquad (2)$$

where n is the order of the reaction.

The activation energy E_{act} determined from the slope of dependence

$$lg\ k = f\ (1/T),$$

obtained by taking the logarithm of the Arrhenius equation (1). To determine the reaction rate constant k, we need to conduct a series of experiments at different temperatures under isothermal conditions with continuous recording of the mass loss.

To determine the apparent activation energy for solid-phase reactions, in terms of heating the reactants at a constant speed by using DTA.

Thermal and thermo gravimetric analysis is widely used to study phase transitions, dissociation reactions, reduction, oxidation, dehydration, and the like, i.e. processes associated with changes in enthalpy and mass of the substance.

The advantage of non-isothermal kinetics methods is that one experiment can determine all the kinetic constants E_{act}, A and n. Defining characteristics of reactions and transformations of these methods are much simpler than the classical gravimetric method, carried out under isothermal conditions. However, the reliability of the

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kinetic analysis in the presence of an additional variable (temperature) requires increased accuracy and a thorough statistical analysis of the data, since the experimental errors can play an important role [2].

Processing curves DTA enables one to determine the activation energy processes. Most of these methods is related to the selection of the values of n and is accompanied by laborious calculations. Furthermore, in the investigation of processes proceeding with participation of chemically impure substances, such as natural materials of complex composition (ores, minerals, etc.) to determine the order of reaction is not possible.

To study the metallurgical processes in which the mass loss (decomposition of carbonates, carbothermic metal reduction, etc.) methods of non-isothermal kinetics, it is proposed to treat the derivatograms by determining the conversion of mass loss and the enthalpy change for the peak area of the thermal effect. However, the application of this method is limited by the processes occurring with weight loss, and do not apply to solid-state reactions without weight loss.

Known study [2], which studied the kinetic regularities of the thermal effect of the reaction, which is measured at the area of the corresponding peak of the DTA. Accurate measurement of the area usually difficult, since the descending branch of the DTA curve does not always come out on the zero line, so that it is necessary to apply different methods of limitations. Various methods of limiting the area lead to discrepancies in the results, reaching 20 % and, as a consequence, reduced accuracy in the determination of the apparent activation energy.

These and other arguments were the cause of finding a way to determine the apparent activation energy for one derivatograms not included in calculation of the peak area of the DTA, shape index curve, the reaction order. The basic equation of non-isothermal kinetics of solid state reactions has the form

$$da/dT = (A/b)[f(a)]e^{-E/RT}; \quad f(a) = (1 - a)^n \quad (3)$$

Equation (1) is obtained from the formal - solid-state reaction kinetic equation

$$da/d\tau = k(1 - a)^n \quad (4)$$

the temperature dependence of the rate constant, the so-called Arrhenius equation

$$k = A \cdot e^{-E/RT} \quad (5)$$

and the temperature equation with a constant heating rate

$$T = T_o + b^\tau, \; dT/d^\tau = b, \quad (6)$$

where a - conversion, n - the order of the reaction, E - activation energy, A - pre-exponential factor, b - heating rate.

The amount of deflection in the first approximation is determined by the formula [2]

$$\Delta t = \Delta S * da/d\tau, \quad (7)$$

where ΔS - the area enclosed by the DTA curve when it deviates from the baseline and return to her.

Indeed, in the initial part of the substance of transformation DTA curve deviation from a given direction is determined only when the rate of reaction.

If the logarithms of expression (8) taking into account equation (4), we obtain the expression

$$lg^{\Delta t} = C + ln(1 - a) - E_{act}/RT, \quad (8)$$

where $C = \Delta S \dfrac{A}{b}$ - factor that unites all the permanent members of equations (4) and (8).

For small values, and the value of nln (1-a) can be neglected and the equation (9) takes the form:

$$lg^{\Delta t} = C - E_{act}/RT \quad (9)$$

Using equation (9), which relates the deviation of the differential recording from the zero position with an apparent activation energy, it is possible to calculate the value E_{act} the slope of the line depending on the deviation from the baseline of the DTA curve in the coordinates lg - 1 / T.

The basis of this method on the assumption that, in the heat at a constant rate value of the degree of heat absorption system in the region from the beginning and the maximum fixed by the development process, proportional to the rate constant of the conversion for each temperature under isothermal conditions. Indeed, as the authors [3], the analysis of thermal effects in exothermic reactions must be taken into account the fact that the maximum point of the DTA curve coincides with the completion of the reaction, so in practical calculations it is necessary to use not more than 50 % of the peak.

EXPERIMENTAL

Experimental study of the reaction of the sample CuMoO$_4$ + C, showed that the reducing agent can be used as carbon and use the method of calculating the interaction of E_{act} CuMoO$_4$ + C in the solid phase occurring during the synthesis of the reinforcement. As the reducing agent used Shubarkul special coke, a carbon content of 95 %.

For the possibility of the reaction CuMoO$_4$ + C is necessary to roasting of molybdenum concentrate. Roasting is performed by applying the humidified air, instead of the traditional dry air in the laboratory of the shaft furnace (Figure 1).

Oxidation firing was carried out to remove sulfur as a contaminant. The liberated hydrogen sulphide is reacted with oxygen, sulfur dioxide, higher oxides of iron, which leads to the regeneration water and removing sulfur:

$2 H_2S + O_2 = 2 H_2O + S_2\uparrow$
$2 H_2S + SO_2 = 2 H_2O + 3/2S \uparrow$
$2 H_2S + Fe_2O_3 \rightarrow 2 FeO (Fe_3O_4) + 2H.$

DTA curves obtained derivatograph Q - 1 500, in the temperature range 25 – 675 °C and a heating rate of 2 mm / min. Pre-weighed, crushed sample in an amount of 1 g was placed in a corundum crucible. Then the sample was sent to the kiln. A sample was measured temperature (T), the weight change Thermo-gravito-
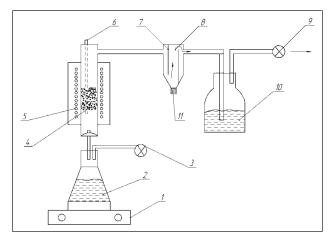
Figure 1 Laboratory tubular shaft furnace
1- plate; 2- water at a temperature of 100 °C; 3- compressor 0,8 m/s air; 4- concentrate pellets; 5- quart tube diameter 50 mm; 6- thermocouple; 7- partition; 8 water-cooled condenser chamber; 9-vacuum pump; 10- water; 11- arsenic sulphides (powder)
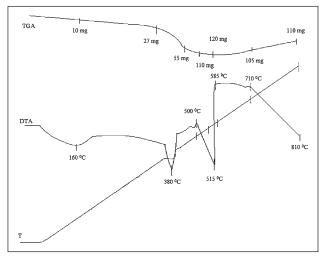
Table 1 **The value of the apparent activation energy**

Temperature range / °C	equation	R	$E_{act.fact.}$ / kJ/ mol
25 °C to 450 °C	y=0,3745x + 2,449	0,975	4,47
500 °C to 560 °C	y=7,4885x - 9,049	0,957	13,43
575 °C to 675 °C	y=13,612x - 15,014	0,972	24,12

which the tangent of the angle dependence of the activation energies E_{act}. (Figure 3)

The same method, calculations for the two remaining peaks derivatograms.

The activation energy of the second peak is equal to 13,43 kJ / mol is characteristic of the reduction reaction (Figure 4).

The activation energy of the third peak is equal to 24,12 kJ / mol is acceptable to the reduction reaction (Figure 5).

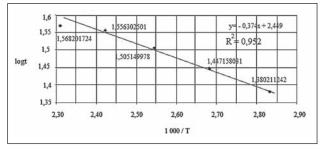Thus, the calculated values of the apparent activation energy of the reaction demonstrated the possibility

Figure 2 TGA and DTA of sample CuMoO₄ + C, taken off in a temperature range from 25 °C to 675 °C

metric Analysis (TGA) and the heat content change (DTA) of the analyte in function of time (Figure 2).

Observed when the sample is heated CuMoO₄ + C endotherm in the temperature range from 25 °C to 450 °C indicates recovering molybdenite copper and removing the natural moisture (Figure 2)

$$CuMoO_4 + C \rightarrow CuMoO_3 + CO.$$

In the temperature range from 575 °C to 675 °C is a partial recovery of molybdenite copper. In the temperature range from 500 °C to 560 °C is a restoration of MoO₂ to MoO.

Based on DTA analysis calculated the activation energy of a sample CuMoO₄ + C (see Table 1).

The result obtained is the activation energy of the first peak of 4,47 kJ / mol for the reduction reaction is acceptable.

To verify the calculations, we construct a graph of lg Δt - ordinate and 1 000 / T - on the horizontal axis, of

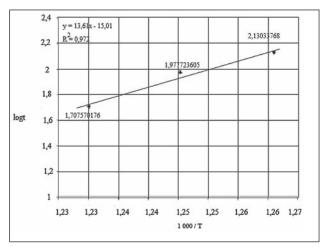**Figure 3** The endothermic effect from 25 °C to 450 °C

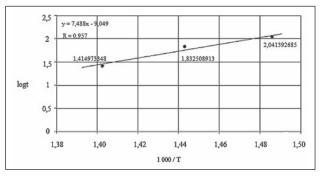**Figure 4** The endothermic effect from 500 °C to 560 °C

Figure 5 The endothermic effect from 575 °C to 675 °C

CuMoO$_4$ + C, to produce individual commercial products of copper and molybdenum oxide.

Activation energy has a small figure of the flow of heat, and thus require much less money and energy for commodity products, which is very important on an industrial scale, this is something to aspire to all enterprises - reduce the cost of the manufactured product.

CONCLUSIONS

This method, determination of the apparent activation energy (CuMoO$_4$ + C) on the DTA curve was used for the detection of exo and endothermic effects and their causes. The results obtained are activation energies indicate a positive reaction.

Samples were characterized by an interval endothermic effect the recovery process. In this same temperature range as there is a sharp decrease in the number of sample and the maximum speed of the process.

Scientific novelty of this research for the first time use of carbon as a reducing agent in the processing of molybdenum concentrates. The studies received commodity products copper and molybdenum oxide, which was the purpose of the work.

LITERATURE

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Note: The responsible for English language is Askakova Assel, Karaganda, Kazakhstan