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ABOUT CORRELATION THERMODYNAMICS AND KINETIC PARAMETERS AT RESEARCH OF PROCESSES CHLORIC METALLURGIES

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Thermodynamic evaluation of the probability of behavior of magnesium and titanium oxides chlorination reaction is realized. At base of research results it has been shown that chlorination mechanism and kinetics regularities may not always correspond to the conclusions made based on the thermodynamic calculations.

Key words: chlorinating, mechanism of reaction, thermodynamics calculations, Gibbs energy, kinetics, speed of chlorinating, diffusion
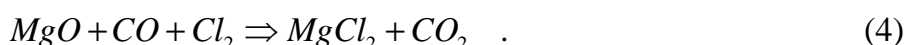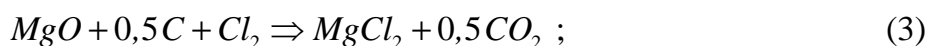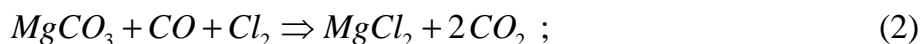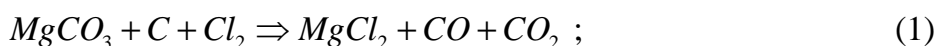
In the last decade in literature interest increases to scientific researches and technological developments is усиливается. At the basis of the use of chlorinating method for dissection of oxide ores and concentrates. Thus authors simply depend upon the conclusions of thermodynamics calculations, which, however, at raising of more thin experiments, confirmed not always, and the real mechanism of flowing physical and chemical transformations is beyond the counted equations of reactions [1,2].

The purpose of work is an analysis of display for these conformities to law, determination of schemes of possible deviations from thermodynamics calculations and stoichiometrical flow of reactions the account of which can promote at raising and realization of future researches.

For realization of thermodynamics researches the thermodynamics calculations of change for Gibbs energy and equilibrium constants for reactions of chlorinating are executed. A maximum temperature which calculations are conducted to is limited by size 1000 °C, coming from the practical range of the carried out processes.

The process of chlorinating for magnesium carbonate the natural mineral of which (magnesite) is used in industrial practice of chlorinating is select the object of thermodynamics researches.

Possibility of flowing of reactions is analyzed:

$$MgCO_3 + C + Cl_2 \Rightarrow MgCl_2 + CO + CO_2 \; ; \tag{1}$$

$$MgCO_3 + CO + Cl_2 \Rightarrow MgCl_2 + 2CO_2 \; ; \tag{2}$$

$$MgO + 0,5C + Cl_2 \Rightarrow MgCl_2 + 0,5CO_2 \; ; \tag{3}$$

$$MgO + CO + Cl_2 \Rightarrow MgCl_2 + CO_2 \quad . \tag{4}$$

Charts of dependences for change of Gibbs energy from a temperature in the considered temperature diapason for all four reactions are direct, lying in area of negative values from -119 to -318 kJou/mole.

As follows from the got dependences, the reactions of chlorinating for both carbonate and oxide magnesium are thermodynamics credible. Motion of change of Gibbs energy for reactions (1)-(4) shows that at temperatures to 714 °C (temperature of melting for $MgCl_2$) thermodynamics preferably chlorinating for carbonate and oxide magnesium with use of gaseous repairer. With the height of temperature higher 714 °C the reactions of chlorinating for carbonate and oxide magnesium are more credible with the use of hard repairer. Formation of magnesium chloride as a result of co-operation at reactions (1)-(4) thermodynamics possibly on all considered range of temperatures, including in a low temperature area.

Experimental researches of mechanism for reaction of co-operation of magnesite with gas mixture of chlorine and carbon oxide showed the row of substantial deviations from thermodynamics prognoses.

At first, low temperature chemical co-operation between magnesite and reactionary gases does not take place. The curves of heating for carbonate show at the current of reactionary gases, that co-operation in the system begins after flowing of dissociation for carbonate which is observed in the interval of temperature 620-660 °C. Further motion of reaction is determined by speeds of heating for the system and serve of reactionary gases.

Secondly, specific speed of chlorinating with the use of mixture ($CO+Cl_2$), attained on the pilot setting at temperature 950-1000 °C, approximately at three times exceeded speed of chlorinating with a hardphase repairer, despite on that thermodynamics dependences specify on advantages of conduct with a hard repairer in this temperature interval.

On the basis of the set diffusive nature the limiting stage of process is certain a transport of gas reagents to the surface of oxide. It is shown theoretical and experimental researches that in accordance with nature of reagents, for achievement maximal speed of chlorinating and degree of the use of chlorine surplus is needed excess of oxide carbon in reactionary mixture that provides equality of diffusive streams of reagents, which is not executed at stoichiometrical correlation of gases.

Thus, researches of mechanism and kinetics for magnesite chlorinating allowed substantially deepening and specifying the aspect on conformity to law flows of process, offered by thermodynamics calculations.

At the analysis of dioxide titanium chlorinating process the calculation of thermodynamics descriptions was executed for reactions

$$2TiO_2 + 3C + 4Cl_2 \Rightarrow 2TiCl_4 + 2CO + CO_2 ; \tag{5}$$

$$TiO_2 + 2CO + 2Cl_2 \Rightarrow TiCl_4 + 2CO_2 ; \tag{6}$$

$$3TiO_2 + 4FeCl_3 \Rightarrow 3TiCl_4 + 2Fe_2O_3 . \tag{7}$$

Correlation of sizes for change of free energy reactions for dioxide titanium chlorinating shows that on all investigational temperature interval more preferable is a reaction of chlorinating with participation a hard repairer, what gaseous. Flow of

process with participation the chlorides of iron is thermodynamics improbably.

At the analysis of experimental researches most authors marked that the process of dioxide titanium chlorinating have diffusive nature, his speed is controlled by the transport of chlorine to the surface of oxide, and a repairer participates on the second stage, at moving away from fusion of the distinguished oxygen. Thus, at chlorinating of titanic slags in fusions there is considerable catalyzed influence of chlorides for variable valency, including. connections of iron. The coefficients of diffusion of ions of Fe^{3+} were measured it is shown that in accordance with the model of complex structure for molten salts, really the transport of chlorine to the surface of dioxide titanium is carried out mainly by the way of stoker transmission drift of complex groupments $[FeCl_4]^-$, freeing an active chlorine on the surface of oxide. In future, the same conformity to law is confirmed and at chlorinating of tantalite-columbite concentrate. However, to produce thermodynamics calculations, based on participation in the process of ions $[FeCl_4]^-$ presently is not possible from insufficient studied of ion $[FeCl_4]^-$ and absence of measuring for his thermodynamics descriptions.

Thus, a thermodynamics estimation of flow is incomplete, and the real mechanism is determined by speed of the intermediate stages of transport for reagents and catalytic participating in him admixtures.

Conclusions. At co-operation of simple binary reagents takes place suffice probability for coincidence of conclusions of thermodynamics calculations and kinetic researches is high. At the study of co-operations for more difficult connections observed deviation from the calculation scheme for flowing of reactions, primary dissociation of reagents is possible on constituents or intermediate foods, and further opening out of process of co-operation with participation more simple connections. Conformity to law of mechanism for realization of process, transport of reagents in a reactionary zone, can to add corrections in their stoichiometrical correlation at equations of reactions, to require one surplus of reagents for more complete realization of process.

LIST OF LITERATURE

1. *Петухов, М. А.* Исследование процесса хлорирования танталито-колумбитового концентрата [Текст] / М. А. Петухов, Н. Н. Ракова, А. В. Чуб // Известия вузов. Цветная металлургия. – 2007. – № 3. – С. 36-45.
2. Хлорирование диоксида гафния газообразным хлором в присутствии углерода [Текст] / *Я. С. Батаев*, Ю. П. Зайков, Ю. А. Лохмотко [и др.] // Известия вузов. Цветная металлургия. – 2010. – № 4. – С. 33-40.