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THE INFLUENCE OF THE PARTIAL PRESSURE OF OXYGEN ON THE PHASE STABILITY IN THE SYSTEM Ca - Cr - O

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ABSTRACT

DTA and TG measurements in controlled atmosphere were used for evaluation of temperature dependence of standard Gibbs energy of reaction
$4/3\ CaCrO_4 + 2/3\ Cr_2O_3 — 4/3\ CaCr_2O_4 + O_2$

INTRODUCTION

The stability of chromium ions Cr^{3+}, Cr^{6+}, Cr^{5+} and Cr^{4+} is depend on the temperature, partial pressure of oxygen in surrounding atmosphere and content of Ca^{2+} ions. E.g. the phase $CaCr_2O_4$ is very good refractory material with high resistance to atmosphere containing oxygen. Addition of Ca^{2+} ions causes the drop of temperature of liquid phase formation from 2443 K to 1295 K. This phenomenon is caused by oxidation $Cr^{3+} \longrightarrow Cr^{6+}$. The phases $Ca_{10}(Cr^{V}O_4)_6(Cr^{VI}O_4)$ and $Ca_5(Cr^{IV}O_4)_2(Cr^{VI}O_4)$ with melting temperatures 1528 and 1548 K are formated at higher content of Ca^{2+} ions. Structures of these phases were studied in works[1,2] and achieved results showed the presence of five and four valent chromium ions. The formation of these phases is connected with control of oxygen content in atmosphere and the dependeces of equilibrium partial pressures on the temperature were measured in works[3-5] and evaluated as temperature dependences of standard Gibbs energies of reactions

$$2/3\ CaCr_2O_4 \longrightarrow 2/3\ CaO + 4/3\ Cr + O_2 \qquad (1)$$

$$\Delta G^o_{r,1} = -165.2 \times T + 790\ 000\ J/mol$$

$$7/10\ Ca_{10}(CrO_4)_7 \longrightarrow 13/10\ Ca_5(CrO_4)_3 + 5/10\ CaCr_2O_4 + O_2 \quad (2)$$

$$\Delta G^o_{r,2} = -139.1 \times T + 250\ 507\ J/mol$$

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$$4/5\ Ca_5(CrO_4)_3 \longrightarrow 6/5\ CaCr_2O_4 + 14/5\ CaO + O_2 \qquad (3)$$

$$\Delta G^o_{r,3} = -298.2 \times T + 489\ 236\ \text{J/mol}$$

This system of equations can be completed by the dependence of standard Gibbs energy of reaction

$$4/3\ CaCrO_4 + 2/3\ Cr_2O_3 \longrightarrow 4/3\ CaCr_2O_4 + O_2 \qquad (4)$$

on the temperature and achieved results can determinate the stability field of six valent chromium Cr^{6+}, which is dangerous for human health, but on the other hand the three valent chromium is very effective refractory material for metallurgy. From these results is possible is possible by convenient conditions at preparation brake escaping of vapours containing Cr^{6+}.

MEASURING METHODS

The measurements were performated in Derivatograph Q 1500-D with additional equipment for partial pressure of oxygen evaluation. Diagram of experimental plant is shown in Fig. 1.

The sample 2 was situated near the oxygen measuring cell 15, which was produced from ZrO_2 with 15 mol. % CaO. The output of electrical signal from this ionic conductor was saved by the platinum layer on the walls of ceramic. The reference electrode was air produced by air pump 13. The partial pressure of oxygen was calculated from a relation

$$p_{O_2} = p_{ref} \exp\left(\frac{4\ F\ E}{R\ T}\right) \qquad (5)$$

where p_{ref} is partial pressure of oxygen in a reference gas, F Faraday constant, R gas constant, T temperature and E open-circuit potential .

DTA and TG effects were correlated with temperatures and partial pressures of oxygen and by this way was achieved the temperature dependence of equilibrium oxygen partial pressure of reaction (4) and further the standard Gibbs energy of reaction (4) was calculated.

The phase stability was verified by static experiments with rapid quenching. The phase analysis was performated by X-ray (Phillips 1540 , Cu K α)

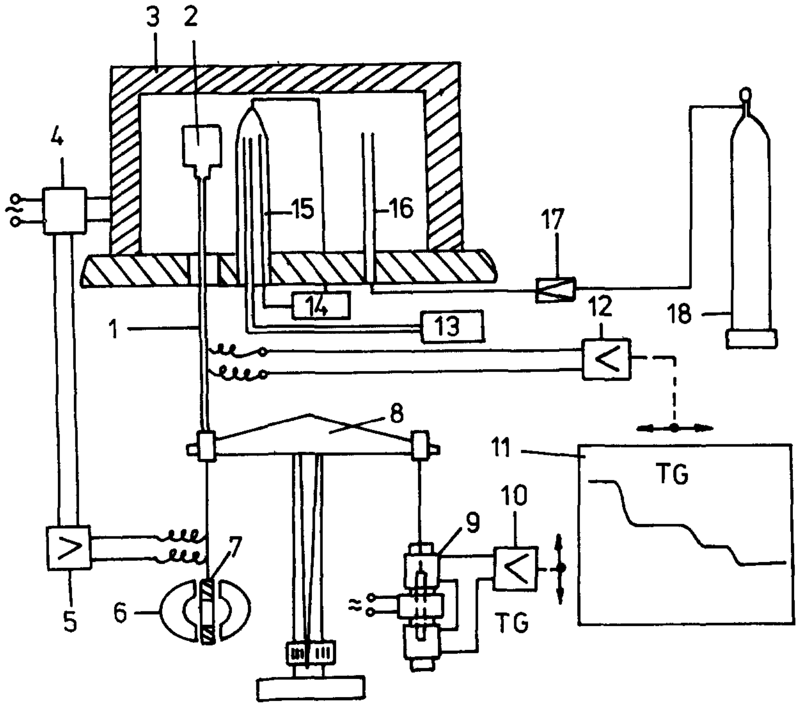

Fig. 1. Experimental plant
1 - sample holder, 2 - sample 3 - furnace, 4 - temperature control, 5, 10 12 - amplifiers, 6 - magnet 7 spool, 8 - gauge, 9 - differential transformer 11 - recorder, 13 - air pump, 14 - voltmeter, 15 - measuring cell, 16 - gas input, 17 - valve, 18- gas container

RESULTS AND DISCUSION

The temperature dependence of standard Gibbs energy of reaction (4) can be writen as linear dependence

$$\Delta G^{o}_{r,4} = -172.0 \times T + 234\,750 \quad \text{J/mol} \qquad (6)$$

We assumed, that the standard enthalpy and standard entropy of reaction (4) is constant in temperature range 700 - 1300 K and their values are

$\Delta H^{o}_{r,4}$ = 234.750 kJ/mol
$\Delta S^{o}_{r,4}$ = 172 $J.mol^{-1}.K^{-1}$

The achieved results allowed to evaluate the Gibbs energy of formation of $CaCr_2O_4$

$$\Delta G^{o}_{r,i} = \sum \nu_j \Delta G^{o}_{f,j} \qquad (7)$$

where i is equal 1 - 4 and $\Delta G^{o}_{f,j}$ are Gibbs energies of formation of phases j .

On the basis of the results is possible estimate conditions for formation of six valent chromium. E.g. $CaCr_2O_4$ can formate at partial pressure of oxygen about 10^{-5}Pa only up to temperature about 650 K. We can assume , that rate constant of this reaction is low and formation of $CaCrO_4$ is slow. At higher partial pressure of oxygen about 1 Pa is T_{eq} for reaction of formation of $CaCrO_4$ equal 850 K. These values are highest temperatures at desired partial pressure of oxygen, where $CaCrO_4$ exists and at these temperatures is oxidation process in equilibrium and driving forces are equal to zero.

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