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Původní práce

PHASE EQUILIBRIA IN THE SYSTEM $CaCr_2O_4$—$Ca_2Fe_2O_5$ UNDER REDUCED PARTIAL PRESSURE OF OXYGEN

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The rapid quenching method was used for determining the phase conditions in the system $CaCr_2O_4$—$Ca_2Fe_2O_5$ *in argon under the partial oxygen pressure of 110 Pa in the temperature interval from 1260 to 1520 °C. The lowest temperature of the appearance of liquid phase was determined at 1405 ± 5 °C, and the formation region of* $Ca(Cr_2Fe)_2O_4$ *solid solution and the region of coexistence of* $Ca(Cr, Fe)_2O_4$, $Ca_2Fe_2O_5$ *and* CaO *were established. A pseudobinary phase diagram of the given system was constructed on the basis of the results obtained.*

INTRODUCTION

Serious study into the corrosive effects of slags on refractories requires knowledge of the physical properties of refractory materials as well as important information on chemical equilibria at various temperatures and various partial pressures of oxygen, because chemical corrosion is caused by reactions between components contained in liquid and solid phase. On the basis of tabellated equilibrial data, or very often by means of phase diagrams, it is possible to delimit the stability regions of the individual phases.

In the case of systems where a significant part is played by the partial pressure of oxygen, one should also take it into account apart from composition and temperature. At partial oxygen pressures close to that in air atmosphere and at temperatures up to 1500 °C, it is possible that in the system CaO—Cr_2O_3—Fe_2O_3, trivalent chromium may be oxidized to hexavalent chromium on the one hand, and Fe^{3+} may be reduced to Fe^{2+} on the other. No ternary diagram of the given system has so far been published. In study [1], which was concerned with rendering the phase diagram of the system $CaCr_2O_4$—$CaFe_2O_4$ more precise, it has been shown that the similar structures, the closely similar values of elementary cell constants for calcium chromite and calcium ferrite [2] as well as the analogous character of the bonds were jointly responsible for the formation of a continuous series of type $Ca(Cr, Fe)_2O_4$ solid solutions. As has been proved in [3], such a solid solution is also formed in the system $CaCr_2O_4$—$Ca_2Fe_2O_5$:

$$\frac{1}{2}\,Ca_2Fe_2O_5 + \frac{1}{2}\,CaCr_2O_4 + \frac{1}{8}\,O_2 \rightarrow \frac{1}{4}\,Ca_4Cr_{4-2x}Fe_{2x}O_{11} + \frac{1}{2}\,CaFe_{2x}Cr_xO_4 \tag{1}$$

while the Ca^{2+} ions enter the phase $Ca_4(Fe, Cr)_4O_{11}$, in which some of the chromium obviously exists in the hexavalent form [4]. When considering the chromium to occur in oxidation degrees 3+, and 6+, the compound $Ca_4(Fe, Cr)_4O_{11}$ can be written in the form 12 CaO . 5 (Fe, Cr)$_2$O$_3$. 2 CrO$_3$. This follows from the fact that owing to their size, the Fe^{3+} ions can be replaced solely by the Cr^{3+} ions in the structure. It is thus possible to assume that on decreasing the partial oxygen pressure in the ambient atmosphere, the proportion of hexavalent chromium in the given system will decrease together with the amount of the phase Ca$_4$(Fe, Cr)$_4$O$_{11}$.

EXPERIMENTAL

The reactions and phase equilibria were investigated by the static method by heating the specimens in an argon atmosphere with a known oxygen content in the temperature range from 1260 to 1520 °C.

The specimens of $Ca_2Fe_2O_5$ with a content of 1 to 90 mole % $CaCr_2O_4$ were prepared from aqueous solutions of calcium nitrate, ammonium bichromate and ferric nitrate (A. R. Merck) using the procedure described in [3]. The specimens were heated in platinum crucibles in a furnace with molybdenum winding in the protective argon atmosphere. The temperature in the working zone of the furnace was measured with a PtRh 30-PtRh 6 thermocouple calibrated at the melting temperatures of gold, palladium and platinum. The content of oxygen in the working atmosphere was determined by an oxygen probe based on zirconium oxide stabilized with about 15 mole % CaO. The time of heating was determined on the basis of preliminary experiments, which have shown that prolonged heating does not affect the phase composition of the test specimens. The specimens were analyzed after rapid quenching. The solid phases were identified by *X*-ray diffraction analysis (the Philips 1540 instrument, Cu K α radiation) using the *X*-ray patterns of calcium chromite, calcium ferrite and calcium oxide. The presence of a liquid phase in the specimens obtained was determined on polished sections in reflected light with the Amplival optical microscope (Zeiss Jena).

THE RESULTS AND DISCUSSION

The results plotted in Table I were used for constructing the pseudobinary phase diagram of the system $CaCr_2O_4$—$Ca_2Fe_2O_5$ for the partial oxygen pressure of 110 Pa under total pressure of 0.1 MPa (Fig. 1). The values of melting temperatures of dicalcium ferrite and calcium chromite obtained in studies [5] and [6] were likewise employed in the construction of the phase diagram. The temperature of the α-β calcium chromite transformation, which is affected by the partial oxygen pressure in the gaseous phase, was calculated using the approximate relationship given in [7].

The system in question is characterized by the temperature of appearance of the liquid phase at 1405 ± 5 °C, below which there is the three-phase field of the coexistence of $Ca_2Fe_2O_5$, CaO and the solid solution Ca(Cr, Fe)$_2$O$_4$. The invariant point at 5 mole % $CaCr_2O_4$ in $Ca_2Fe_2O_5$ was determined on the basis of ananalysis of specimens heated at 1420 °C, using the JXA-5A microanalyzer. Similarly to the air atmosphere, the solubility of calcium chromite in dicalcium ferrite has not been proved at contents exceeding 1 mole %. On the side of calcium chromite, there is the region of co-existence of the solid solution Ca(Cr, Fe)$_2$O$_4$ with CaO. The dashed lines in the pseudobinary diagram indicate the probable courses of the solidus and liquidus lines at temperatures exceeding 1520 °C. It was assumed that at higher temperatures and higher contents of $CaCr_2O_4$ in $Ca_2Fe_2O_5$, the system behaves similarly as in air atmosphere.

Table I

The experimental results

Experiment No.	Temperature t/°C	$CaCr_2O_4$ content C_{CCr} (mole %)	The phases present*)
1	1260	10	CCr, C_2F, C
2	1280	10	CCr, C_2F, C
3	1300	10	CCr, C_2F, C
4	1320	10	CCr, C_2F, C
5	1340	1	CCr, C_2F, C
6	1340	10	CCr, C_2F, C
7	1340	20	CCr, C_2F, C
8	1340	30	CCr, C_2F, C
9	1340	40	CCr, C_2F, C
10	1340	50	CCr, C_2F, C
11	1340	60	CCr, C_2F, C
12	1340	70	CCr, C_2F, C
13	1340	80	CCr, C
14	1340	90	CCr, C
15	1370	1	CCr, C, C_2F
16	1370	10	CCr, C_2F, C
17	1370	20	CCr, C_2F, C
18	1370	30	CCr, C_2F, C
19	1370	40	CCr, C_2F, C
20	1370	50	CCr, C_2F, C
21	1370	60	CCr, C_2F, C
22	1370	70	CCr, C
23	1370	80	CCr, C
24	1370	90	CCr, C
25	1400	10	CCr, C_2F, C
26	1400	20	CCr, C_2F, C
27	1400	30	CCr, C_2F, C
28	1400	40	CCr, C
29	1400	50	CCr, C
30	1410	1	C_2F, L
31	1410	10	CCr, C, L
32	1410	20	CCr, C, L
33	1410	30	CCr, C, L
34	1410	40	CCr, C
35	1410	50	CCr, C
36	1440	10	CCr, L, (C)
37	1440	20	CCr, L, (C)
38	1450	30	CCr, L, C
39	1460	10	L
40	1460	50	CCr, C
41	1500	50	CCr, C
42	1520	50	CCr, L, (C)

*) CCr — $Ca(Cr, Fe)_2O_4$, C_2F — $Ca_2Fe_2O_5$, C — CaO, L — melt

It has been shown that reduced content of oxygen in the argon atmosphere does not permit the phase $Ca_4(Fe, Cr)_4O_{11}$ to be formed, which is in connection with the failure of Cr^{3+} to oxidize to Cr^{6+} at the partial oxygen pressure of 110 Pa at the given temperatures. Formation of the solid solution $Ca(Cr, Fe)_2O_4$, during which Fe^{3+} ions take up the places of Cr^{3+} ions, brings about liberation of one half of the calcium ions which enter the reaction in the form of dicalcium ferrite:

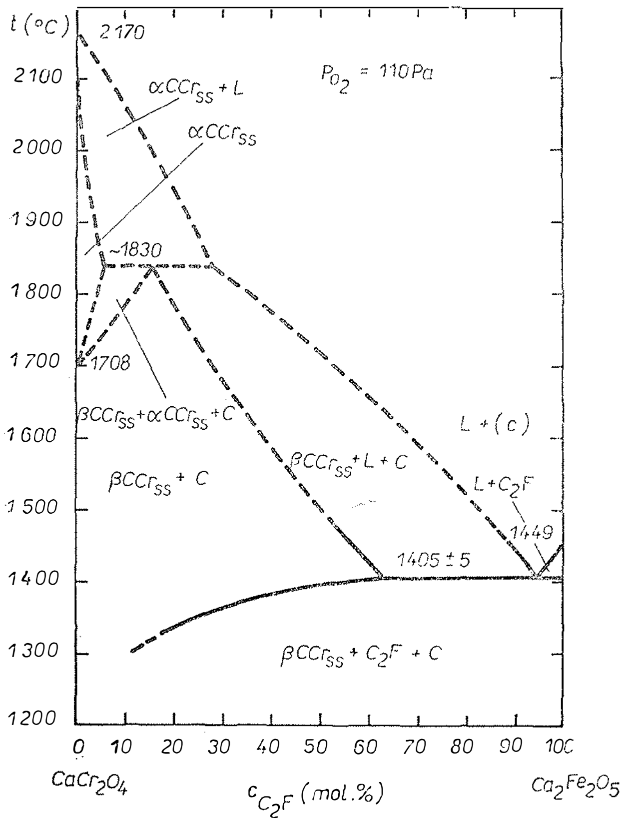

Fig. 1. Pseudobinary phase diagram of the system $CaCr_2O_4$—$Ca_2Fe_2O_5$ *for the partial oxygen pressure* $p_{O_2} = 110$ *Pa.*

$$(1 - x)\, CaCr_2O_4 + x\, Ca_2Fe_2O_5 \rightarrow CaCr_{2(1-x)}Fe_{2x}O_4 + x\, CaO \qquad (2)$$

producing calcium oxide. The maximum CaO content will be obviously situated at the solubility limit of $Ca_2Fe_2O_5$ in $CaCr_2O_4$. The phase diagram obtained indicates that at the solubility limit, where all the dicalcium ferrite present has just been consumed by reaction (2), the CaO content in the temperature range 1340 to 1405 °C increases from about 16 mole % up to 38 mole % CaO. The CaO content in the three-phase region below 1405 °C can be determined on the basis of the knowledge of the initial composition and solubility of $Ca_2Fe_2O_5$ in $CaCr_2O_4$ at the given temperature. It is assumed that in the Ca(Cr, Fe)$_2$O$_4$ solid solution, the Fe^{3+} ions are capable of replacing solely the Cr^{3+} ions, and that Fe^{3+} is not reduced to Fe^{2+}. The presence of a phase containing iron in bivalent form has not been proved.

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FÁZOVÉ ROVNOVÁHY V SÚSTAVE $CaCr_2O_4$ - $Ca_2Fe_2O_5$ PRI ZNÍŽENOM PARCIÁLNOM TLAKU KYSLÍKA

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Metódou náhleho ochladenia sa stanovili fázové rovnováhy v sústave $CaCr_2O_4$ $Ca_2Fe_2O_5$ v argóne s parciálnym tlakom kyslíka 110 Pa v teplotnom intervale 1260 až 1520 °C. Na základe výsledkov uvedených v tabulke I sa zostrojil pseudobinárny fázový diagram uvedenej sústavy. Sústava sa vyznačuje teplotou objavenia sa kvapalnej fázy 1405 5 °C. Tvorbou tuhého roztoku typu $Ca(Cr, Fe)_2O_4$ dochádza k vzniku CaO (rovnica [2]), ktorý sa dokázal tak v oblasti koexistencie $Ca(Cr, Fe)_2O_4$ s $Ca_2Fe_2O_5$, ako aj v oblasti tuhého roztoku $Ca(Cr, Fe)_2O_4$. Nad teplotou 1520 °C sa predpokladalo podobné chovanie uvedenej sústavy ako vo vzdušnej atmosfére. Ku konštrukcii fázového diagramu na obr. 1 sa ďalej použili hodnoty teplôt topenia dikalciumferitu a kalciumchromitu, ktoré sa získali v prácach [5] a [6]. Teplota modifikačnej premeny α—β, ktorá je ovplyvnená parciálnym tlakom kyslíka v plynnej fáze, sa vypočítala na základe približného vzťahu uvedeného v práci [7].

Obr. 1. *Pseudobinárny fázový diagram sústavy* $CaCr_2O_4$- $Ca_2Fe_2O_5$ *pre parciálny tlak kyslíka* $p_{O_2} = 110$ *Pa.*

ФАЗОВЫЕ РАВНОВЕСИЯ В СИСТЕМЕ $CaCr_2O_4$—$Ca_2Fe_2O_5$ ПРИ ПОНИЖЕННОМ ПАРЦИАЛЬНОМ ДАВЛЕНИИ КИСЛОРОДА

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Методом резкого охлаждения установили фазовые равновесия в системе $CaCr_2O_4$—$CaFe_2O_5$ в аргоне с парциальным давлением кислорода 110 Па в температурном интервале 1260—1520 °C. На основании результатов, приводимых в таблице I построили псевдобинарную диаграмму упомянутой системы. Система отличается температурой появления жидкой фазы 1405±5 °C. В результате образования твердого раствора типа $Ca(Cr, Fe)_2O_4$ возникает CaO (уравнение [2]), которая была доказана как в области сосуществования $Ca(Cr, Fe)_2O_4$ с $Ca_2Fe_2O_5$, так в области твердого раствора $Ca(Cr, Fe)_2O_4$. Выше температуры 1520 °C предполагали подобное поведение приводимой системы, как и в атмосфере воздуха. Для построения диаграммы фаз на рис. 1 использовали также величины температур плавления дикальцийферита и кальцийхромита, которые были получены в работах [5] и [6]. Температуру модификационного превращения α—β, на которое оказывает влияние парциальное давление кислорода в газовой фазе, рассчитали на основании приблизительного отношения, приводимого в работе [7].

Рис. 1. *Псевдобинарная диаграмма фаз системы* $CaCr_2O_4$ —$Ca_2Fe_2O_5$ *для парциального давления кислорода* $p_{O_2} = 110$ *Па.*