PHASE EQUILIBRIA IN THE SYSTEM $CaCr_2O_4$—$Ca_2Fe_2O_5$

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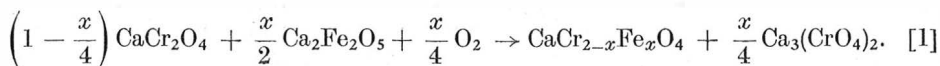*809 34 Bratislava, Dúbravská cesta 5*

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The results of X-ray analysis and microscopical analysis of rapidly quen-
ched samples were used for constructing a pseudobinary phase diagram of the
system $CaCr_2O_4$ — $Ca_2Fe_2O_5$ *in air atmosphere. The peritectic temperature of*
$1830 \pm 10°C$ and the eutectic temperature of $1280 \pm 10°C$ were determined.
At contents exceeding 1 mole % $CaCr_2O_4$ *in the system with dicalcium ferrite*
no solid solutions are formed.

INTRODUCTION

The phase equilibria in the system $CaCr_2O_4$—$Ca_2Fe_2O_5$, which are the subject of the present study, should contribute to wider understanding of mutual solubility, of the shifts in temperature of inversion $\alpha \rightarrow \beta$ $CaCr_2O_4$ taking place in connection with the formation of solid solution $Ca(Cr, Fe)_2O_4$, and of the formation of a liquid phase in the utilization of $CaCr_2O_4$ as lining of technological plant for iron refining. The idea to utilize the compound as a refractory material has been conceived on the basis of its high melting temperature (2170 °C [1]) as well as on that of its suitable chemical and physical properties in the temperature ranges employed in the processing of iron.

According to Berezhnoy [2], co-existence of calcium chromite with Fe_2O_3 and with $Ca_2Fe_2O_5$, $CaFe_2O_4$ and $CaFe_4O_7$ may be expected in the system CaO—Cr_2O_3—Fe_2O_3. A diagram of the system $CaCr_2O_4$—$CaFe_2O_4$, described in literature [3] has been rendered more precise on the basis of the results of studies [4] and [5] and on that of the present author's experimental data published in their previous work [6].

Phase equilibria in the system $CaCr_2O_4$—$Ca_2Fe_2O_5$ were studied by Pyatikop [7] who suggests that in air atmosphere at 1400 °C the phase $Ca_3(CrO_4)_2$ arises besides the solid solution $CaCr_{2-x}Fe_xO_4$ according to the schematic equation

$$\left(1 - \frac{x}{4}\right) CaCr_2O_4 + \frac{x}{2} Ca_2Fe_2O_5 + \frac{x}{4} O_2 \rightarrow CaCr_{2-x}Fe_xO_4 + \frac{x}{4} Ca_3(CrO_4)_2. \quad [1]$$

The presence of the solid solution was established by X-ray diffraction phase analysis and the existence of $Ca_3(CrO_4)_2$ was obviously assumed by the author [7] because it had been at that time the single probable compound which could have formed in air atmosphere with the surplus Ca^{2+} ions.

However, the more recent experiments by Johnson [8] revealed that in mixtures of $CaCr_2O_4$ with $Ca_2Fe_2O_5$ at 1200 °C in air atmosphere some of the Fe^{3+} ions in dicalcium ferrite are replaced with Cr^{3+} ions. By the effect of oxygen, some of the chromium is oxidized producing the phase $Ca_4(Cr, Fe)_4O_{11}$ [8] which contains also chromium ions in oxidation degree 6^+ besides the Cr^{3+} ions.

Information on the existence of a liquid phase is important for practical reasons. In view of the studies [1], [3], [5] and [6], liquid phase may be expected to arise on the $CaCr_2O_4$ side at about 1800 °C, similarly to the case of the system $CaCr_2O_4$—$CaFe_2O_4$ investigated in the previous study [6].

.EXPERIMENTAL

The reactions and phase equilibria were studied by the static method by heating the specimens in air atmosphere at temperatures ranging from 1250 to 1860 °C. The samples of $Ca_2Fe_2O_5$ containing 1 to 95 mole % $CaCr_2O_4$ were prepared from 1 M aqueous solutions of calcium nitrate, ammonium bichromate and ferric nitrate (A. R. Merck). After being mixed in the respective ratios the solutions were evapor-

Table I.

Experimental results

Exp. No.	Temperature °C	$Ca_2Fe_2O_5$ content, mole %	The phases present
1	1200	50	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$
2	1200	60	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$, $Ca_2Fe_2O_5$
3	1200	70	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$, $Ca_2Fe_2O_5$
4	1200	80	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$, $Ca_2Fe_2O_5$
5	1200	90	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$, $Ca_2Fe_2O_5$
6	1200	99	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$, $Ca_2Fe_2O_5$
7	1230	50	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$
8	1230	60	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$, $Ca_2Fe_2O_5$
9	1230	70	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$, $Ca_2Fe_2O_5$
10	1230	80	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$, $Ca_2Fe_2O_5$
11	1230	90	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$, $Ca_2Fe_2O_5$
12	1230	95	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$, $Ca_2Fe_2O_5$
13	1230	99	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$, $Ca_2Fe_2O_5$
14	1260	50	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$
15	1260	60	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$
16	1260	70	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$, $Ca_2Fe_2O_5$
17	1260	80	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$, $Ca_2Fe_2O_5$
18	1260	90	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$, $Ca_2Fe_2O_5$
19	1260	97	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$, $Ca_2Fe_2O_5$
20	1260	99	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$, $Ca_2Fe_2O_5$
21	1270	70	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$
22	1270	95	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$, $Ca_2Fe_2O_5$
23	1270	97	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$, $Ca_2Fe_2O_5$
24	1270	99	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$, $Ca_2Fe_2O_5$
25	1280	80	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$
26	1290	90	$\beta Ca(Cr, Fe)_2O_4$, melt
27	1290	95	$\beta Ca(Fe, Cr)_2O_4$, melt
28	1290	97	$Ca_2Fe_2O_5$, melt
29	1290	99	$Ca_2Fe_2O_5$, melt
30	1300	80	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$
31	1350	80	$\beta Ca(Cr, Fe)_2O_4$, melt
32	1400	60	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$
33	1430	60	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$
34	1450	60	$\beta Ca(Cr, Fe)_2O_4$, melt
35	1500	40	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$
36	1550	40	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$
37	1570	40	$\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$
38	1600	40	$\beta Ca(Cr, Fe)_2O_4$, melt
39	1750	10	$\beta Ca(Cr, Fe)_2O_4$
40	1800	10	$\beta Ca(Cr, Fe)_2O_4$, $\alpha Ca(Cr, Fe)_2O_4$
41	1830	10	$\alpha Ca(Cr, Fe)_2O_4$
42	1860	10	$\alpha Ca(Cr, Fe)_2O_4$, melt

ated dry and heated at 1200 °C. The substances obtained were compacted into pellets 3 mm in diameter. The samples were tempered in platinum crucibles in a furnace with molybdenum winding in protective argon atmosphere. At temperatures above 1700 °C the experiments were carried out in a CENTORR type 10—2068 furnace. The temperature was measured with PtRh30-PtRh6 thermocouples (Safina) and Ir—RhIr40 ones (Heraeus), which had been calibrated at the melting temperatures of gold, palladium and platinum. After 4 hours of firing the specimens were quickly quenched by falling into a copper block. The time of firing was determined on the basis of preliminary experiments which have revealed that heating of samples for periods exceeding 4 hours does not affect their phase composition.

The presence of a liquid phase in the samples was determined on polished sections in reflected light under the AMPLIVAL — Zeiss Jena optical microscope. The solid phases were identified by X-ray diffraction analysis using the Philips 1540 instrument (CuK α radiation) on the basis of literary data [8], [9], and the author's own X-ray patterns of calcium chromite and calcium ferrite.
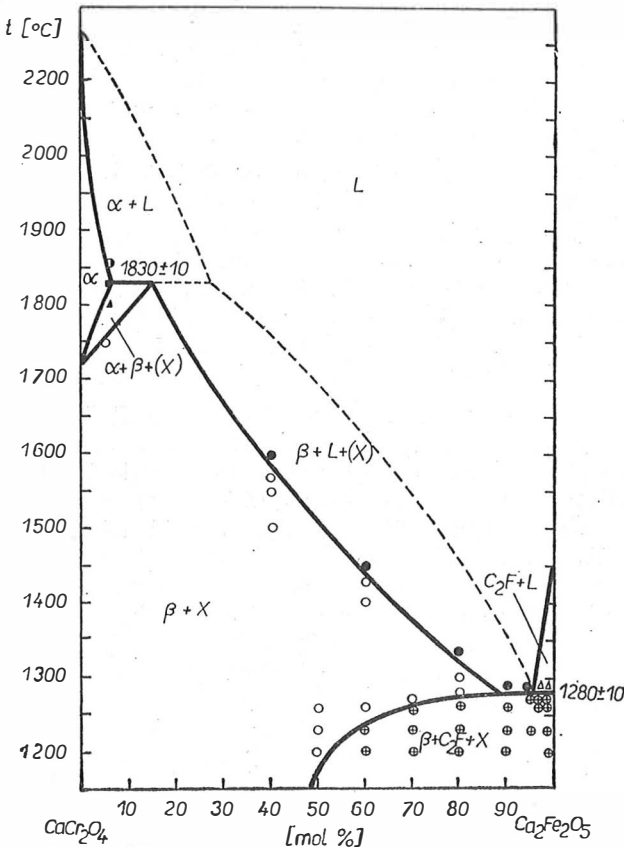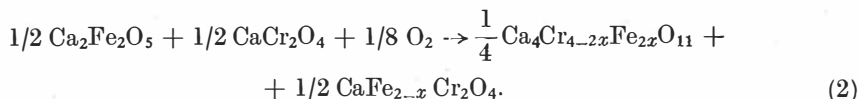

Fig. 1. Pseudobinary phase diagram of the system $CaCr_2O_4 - Ca_2Fe_2O_5$;
$\bigcirc$ — $\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$; $\oplus$ — $\beta Ca(Cr, Fe)_2O_4$, $Ca_4(Fe, Cr)_4O_{11}$, $Ca_2Fe_2O_5$; $\bullet$ — $\beta Ca(Cr, Fe)_2O_4$, melt; $\triangle$ — $Ca_2Fe_2O_5$, melt; $\blacktriangle$ — $\beta Ca(Cr, Fe)_2O_4$, $\alpha Ca(Cr, Fe)_2O_4$ $\blacksquare$ — $\alpha Ca(Cr, Fe)_2O_4$; $\mathbin{\text{\ding{0}}}$ — $\alpha Ca(Cr, Fe)_2O_4$, melt.

THE RESULTS AND DISCUSSION

The results listed in Table 1 and the melting temperatures of $CaCr_2O_4$ and $Ca_2Fe_2O_5$ specified in [1] and [4] were used for constructing the phase diagram shown in Fig. 1. This is a pseudobinary diagram of the system $CaCr_2O_4-Ca_2Fe_2O_5$ for partial oxygen pressure $P_{O_2} = 0.021$ MPa in the gaseous phase.

In the given system, Cr^{3+} is oxidized to Cr^{6+} in air atmosphere. This reaction obviously results from the excess Ca^{2+} ions which arise during formation of the $Ca(Cr, Fe)_2O_4$ solid solution. The presence of $Ca(Fe, Cr)_4O_{11}$ has been confirmed by X-ray diffraction analysis. Formation of this phase can be described by the schematic equation

$$1/2\ Ca_2Fe_2O_5 + 1/2\ CaCr_2O_4 + 1/8\ O_2 \rightarrow \frac{1}{4} Ca_4Cr_{4-2x}Fe_{2x}O_{11} +$$
$$+ 1/2\ CaFe_{2-x}\ Cr_2O_4. \tag{2}$$

For the reasons given above, the number of components in the given system and thus also the number of the possible co-existing phases have thus increased. The indexes x in schematic equation (2) cannot be varied arbitrarily. In the formula of the first phase on the right-hand side of the equation the content of Cr^{6+} ions cannot formally fall below a certain limit, and simultaneously it is obviously ruled out that the entire amount of Cr ions would be present as Cr^{6+}.

In Fig. 1 the conditions in the system $CaO-Fe_2O_3-Cr_2O_3-CrO_3$ are represented in a pseudobinary diagram which has practical importance for assessing the conditions for existence of a liquid phase. The presence of the phase $Ca_4(Fe, Cr)_4O_{11}$ may be assumed even above the solidus temperature even when it has not been explicitly determined by X-ray diffraction analysis. Presence of the given phase is controversial with the results by Pyatikop [7] according to whom the phase $Ca_3(CrO_4)_2$ is formed under the given conditions. On the other hand, the results of the present study are in an agreement with those by Johnson [8].

The diagram indicates that similarly to the system $CaCr_2O_4-CaFe_2O_4$, with increasing content of Fe^{3+} ions in the structure of calcium chromite, the low-temperature β form is stabilized into the higher temperature region. Both instances show the same peritectic temperature of 1830 ± 10 °C while the composition of the peritectic point amounts to about 16 mole % $Ca_2Fe_2O_5$. From identical values of peritectic temperature in this system and in the system $CaCr_2O_4-CaFe_2O_4$ it follows that the presence of the phase $Ca_4(Cr, Fe)_4O_{11}$ is not marked at higher $CaCr_2O_4$ contents. Formation of solid solutions has not been established on the dicalcium ferrite side at concentrations exceeding 1 mole % $CaCr_2O_4$. Experiments have shown that in the given system in air atmosphere no liquid phase appears at temperatures up to 1280 ± 10 °C, while the eutectic point composition amounts to about 4 mole % $CaCr_2O_4$. In the subsolidus region there is a region of 3-phase co-existence of $Ca(Cr,Fe)_2O_4$, $Ca_2Fe_2O_5$ and $Ca_4(Cr,Fe)_4O_{11}$ below the eutectic temperature.

From the standpoint of practical utilization of calcium chromite under industrial conditions, where the linings are exposed to the effects of gaseous phase containing oxygen at about 10^{-5} Pa during processing of iron, it will be necessary to carry out experiments even at lower partial oxygen pressures. It may be expected that formation of $Ca_4(Fe,Cr)_4O_{11}$ will be suppressed and the solubility of $Ca_2Fe_2O_5$ in $CaCr_2O_4$ is going to be reduced at a lower oxygen content in the gaseous phase.

CONCLUSION

The system CaCr$_2$O$_4$—Ca$_2$Fe$_2$O$_5$ was studied in air atmosphere in the temperature interval of 1200 to 1860 °C. A pseudobinary phase diagram has been constructed on the basis of results of X-ray diffraction analysis and microscopical analysis of rapidly quenched specimens. Similarly as in study [6], the temperature of the $\alpha-\beta$ inversion increases with increasing content of Fe^{3+} ions in the calcium chromite structure. It has been proved that formation of the compound Ca$_4$(Fe,Cr)$_4$O$_{11}$ does not significantly affect the character of the subsolidus region close to pure calcium chromite.

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FÁZOVÉ ROVNOVÁHY V SÚSTAVE CaCr$_2$O$_4$—Ca$_2$Fe$_2$O$_5$

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Metódou náhleho ochladenia vzoriek sa študovala sústava CaCr$_2$O$_4$—Ca$_2$Fe$_2$O$_5$ vo vzdušnej atmosfére v teplotnom intervale 1200 až 1860 °C. Na základe výsledkov rtg. difrakčnej a mikroskopickej analýzy uvedených v tabuľke 1 sa zostrojil pseudobinárny fázový diagram na obr. 1. V subsolidusovej oblasti sa vedľa tuhých roztokov α-Ca(Cr, Fe)$_2$O$_4$ a β-Ca(Cr, Fe)$_2$O$_4$ a Ca$_2$Fe$_2$O$_5$ uvádza fáza Ca$_4$(Fe, Cr)$_4$O$_{11}$, ktorá bola popísaná v práci [8]. Vznik fázy vyjadruje reakčná schéma (2), z ktorej je zrejmé, že o priebehu reakcie rozhoduje obsah kyslíka v okolitej atmosfére.

Stanovila sa peritektická teplota 1830 ± 10 °C a eutektická teplota 1280 ± 10 °C. Pri obsahoch vyšších ako 1 mol. % CaCr$_2$O$_4$ v sústave s dikalciumferitom sa netvoria tuhé roztoky.

Obr. 1. Pseudobinárny fázový diagram sústavy CaCr$_2$O$_4$—Ca$_2$Fe$_2$O$_5$; ○ — βCa(Cr, Fe)$_2$O$_4$, Ca$_4$(Fe, Cr)$_4$O$_{11}$; ⊕ — βCa(Cr, Fe)$_2$O$_4$, Ca$_4$(Fe, Cr)$_4$O$_{11}$, Ca$_2$Fe$_2$O$_5$; ● — βCa(Cr, Fe)$_2$O$_4$, tavenina; △ — Ca$_2$Fe$_2$O$_5$, tavenina; ▲ — βCa(Cr, Fe)$_2$O$_4$, α(Ca(Cr, Fe)$_2$O$_4$; ■ — αCa(Cr, Fe)$_2$O$_4$; ◐ — — αCa(Cr, Fe)$_2$O$_4$, tavenina.

ФАЗОВЫЕ РАВНОВЕСИЯ В СИСТЕМЕ CaCr$_2$O$_4$—CaFe$_2$O$_5$

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Методом резкого охлаждения образцов исследовали систему CaCr$_2$O$_4$—Ca$_2$Fe$_2$O$_5$ в среде воздуха в температурном интервале 1200—1860 °C. На основании результатов, полученных с помощью рентгеновского дифракционного и микроскопического анализов,

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приводимых в таблице 1, построили псевдобинарную фазовую диаграмму на рис. 1 В субсолидусовой области кроме твердых растворов $\alpha Ca(Cr, Fe)_2O_4$ и $\beta Ca(Cr, Fe)_2O$ и $Ca_2Fe_2O_5$ приводится фаза $Ca_4(Fe, Cr)_4O_{11}$, которая описывается в работе [8]. Образованию фазы отвечает схема реакции (2), из которой видно, что на ход реакции решающее влияние оказывает содержание кислорода в окружающей среде.

Установили перитектическую температуру 1830 ± 10 °C и эвтектическую температуру 1280 ± 10 °C. При более высоких содержаниях чем 1 мол. % $CaCr_2O_4$ в системе с дикальцийферритом твердые растворы не образуются.

Рис. 1. Псевдобинарная фазовая диаграмма системы $CaCr_2O_4$—$Ca_2Fe_2O_5$; ○ — $\beta Ca(Cr, Fe)_2O_4$. $Ca_4(Fe, Cr)_4O_{11}$; ⊕ — $\beta Ca(Cr, Fe)_2O_4$. $Ca_4(Fe, Cr)_4O_{11}$. $Ca_2Fe_2O_5$; ● — $\beta Ca(Cr, Fe)_2O_4$; *расплав*, △ — $Ca_2Fe_2O_5$, *расплав*; ▲ — $\beta Ca(Cr, Fe)_2O_4$, $\alpha Ca(Cr, Fe)_2O_4$; ■ — $\alpha Ca(Cr, Fe)_2O_4$; ◑ — $\alpha Ca(Cr, Fe)_2O_4$, *расплав*.