PHASE EQUILIBRIA IN THE SYSTEM CaCr₂O₄ — CaFe₂O₄

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The method of rapid quenching was used for determining phase conditions in the system CaCr₂O₄—CaFe₂O₄ in the temperature interval of 1280 to 1830 °C in air atmosphere. The positions of the solidus line were established precisely and the peritectic temperature was found to amount to 1830 ± 10 °C. The probable course of the liquidus line was estimated on the basis of two experimentally obtained values.

INTRODUCTION

As a result of increasing demand for materials resisting high temperatures and corrosive environments, new compounds having high melting temperatures and suitable physical and chemical properties are sought. One of such compounds is calcium-chromite $CaCr_2O_4$ exhibiting a melting temperature of 2170 °C [1] and a high chemical resistance, which renders $CaCr_2O_4$ containing materials promising in the form of refractory lining in plants for processing liquid stell. Some patents [2] — [4] suggest the alpha form of calcium chromite as base material for cast refractories with outstanding thermomechanical and thermochemical properties.

No ternary diagram $CaO—Fe_2O_3—Cr_2O_3$ has so far been published. The system belongs among those the phase composition of which depends considerably on partial pressure of oxygen in the ambient atmosphere. Formation of compounds of CaO with iron oxides and chromium at various oxidation degrees was dealt with in study [5] — [10].

Measurements in air atmosphere were carried out in the binary systems $CaO—Cr_2O_3$ [6—8, 14], $Fe_2O_3—CaO$ [10], $Cr_2O_3—Fe_2O_3$ [11]. On the basis of thermodynamic analysis, Berezhnoy [5] plotted in the ternary diagram regions of co-existence of Fe_2O_3, $CaFe_4O_5$, $CaFe_2O_4$, $Ca_2Fe_2O_7$ and $CaCr_2O_4$. A section along the connecting line $CaCr_2O_4—CaFe_2O_4$ was published by the authors of [12]. This diagram, constructed on the basis of melting temperature of $CaCr_2O_4$ and $CaFe_2O_4$ and using the temperature of modification transformation $\alpha — \beta$ calcium chromite established in study [13] has been supplemented by Berezhnoy [5]. The latter author has used the data from the study by Phillips and Muan [10] who reported on incongruent melting of $CaFe_2O_4$. The temperature of $\alpha — \beta$ modification transformation (1570 °C) taken over by Ford and Rees [12] from study [13] had been determined in a reductive atmosphere. Study [14], verified modification transformation of $\alpha — \beta$ calcium chromite in air takes place at 1720 °C and decreases with decreasing oxygen content in the gaseous phase; it was therefore considered necessary to verify or revise the diagram suggested in paper [5].

The present study had the aim of determining the co-existence region of α and β calcium chromite, peritectic temperature and the co-existence region of α and β $Ca(Cr, Fe)_2O_4$ solid solutions and melt in air atmosphere, which may be of significance for evaluating the interaction of iron compounds contained in slag with refractory lining of technological plants.

EXPERIMENTAL

The phase equilibria were studied by the static method based on rapid quenching of samples. The samples were heated at selected temperature levels within the interval of 1280 to 1830 °C. Samples of $CaCr_2O_4$ with graded contents of 3 to 90 mole % $CaFe_2O_4$ were prepared. The mixtures were prepared from 1 M solutions of calcium nitrate, ferric nitrate and ammonium bichromate (A. R., Lachema, N. C.) in the respective proportions. After evaporation and heating at 1150 °C in air atmosphere the substances obtained were compressed into pellets under a pressure of 10 MPa. The pellets were heated in platinum crucibles in air atmosphere for 4 hours. A furnace with molybdenum winding was used in the experiments. Heating at temperature exceeding 1700 °C was carried out in a type 10-2068 CENTORR furnace. The temperature was measured by PtRh 18 (Safina) and Ir-Ir40%Rh60% (Heraeus) thermocouples, which had been calibrated at melting points of gold, palladium and platinum. After rapid quenching the samples were analyzed by X-ray diffraction, microscopically and by means of the JXA-5A electron microanalyzer.

Table 1

The experimental results

Exp. No	Temperature °C	$CaFe_2O_4$ content, mole %	The phases present*)
1	1280	90	β_{ss}, L
2	1280	80	β_{ss}
3	1310	90	β_{ss}, L
4	1310	80	β_{ss}
5	1340	90	β_{ss}, L
6	1340	80	β_{ss}, L
7	1340	70	β_{ss}
8	1380	90	L
9	1450	60	β_{ss}
10	1460	60	β_{ss}, L
11	1460	80	L
12	1600	40	β_{ss}, L
13	1710	0	β
14	1720	5	β_{ss}
15	1720	20	β_{ss}
16	1730	0	α
17	1780	5	α_{ss}, β_{ss}
18	1780	10	β_{ss}
19	1780	20	β_{ss}, L
20	1810	10	β_{ss}, α_{ss}
21	1830	3	α_{ss}
22	1830	5	α_{ss}, β_{ss}, L
23	1830	10	α_{ss}, L, β_{ss}

*) β_{ss} — $\beta Ca(Cr,Fe)_2O_4$, α_{ss} — $\alpha Ca(Cr,Fe)_2O_4$, L — melt

THE RESULTS AND DISCUSSION

Data from literature [1], [12] and [14] and the experimental results were used for constructing for $p_{O_2} = 0.021$ MPa the pseudobinary diagram shown in Fig. 1. The system is characterized by the formation of a continuous series of solid solutions

composed of β-$CaCr_2O_4$ and $CaFe_2O_4$ as a result of the similarity of the structures [15].

As indicated by the phase diagram obtained by substitution of Fe^{3+} ions for Cr^{3+} ions in β-$CaCr_2O_4$, the latter form is stabilized in the higher temperature region. With increasing content of Fe^{3+} ions in the structure of β-$CaCr_2O_4$, the temperature of its transformation is raised from 1720 °C up to the peritectic temperature of 1830 $\pm$10 °C at a content of about 14 mole % $CaFe_2O_4$. Determination of the region
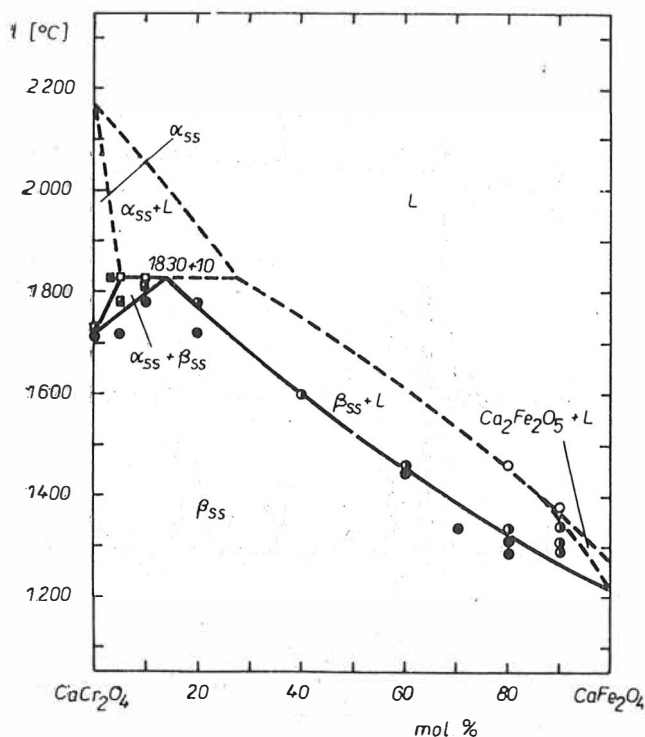

Fig. 1. *Phase diagram of the system* $CaCr_2O_4$—$CaFe_2O_4$; $\bullet$ — β-$Ca(Cr, Fe)_2O_4$; $\circleddash$ — β-$Ca(Cr, Fe)_2O_4$ *and melt*, $\circ$ — *melt*, $\boxtimes$ — α-$Ca(Cr, Fe)_2O_4$ *and* β-$Ca(Cr, Fe)_2O_4$, $\square$ — $Ca(Cr, Fe)_2O_4$ β-$Ca(Cr, Fe)_2O_4$ *and melt*, $\blacksquare$ — α-$Ca(Cr, Fe)_2O_4$.

where α and the β form of $Ca(Cr, Fe)_2O_4$ co-exist, and which separates the single-phase fields of α-$Ca(Cr, Fe)_2O_4$ and β-$Ca(Cr, Fe)_2O_4$ solutions, was carried out on the basis of X-ray phase analysis and is demonstrated on the diffractograms of samples No 18, 20, 21 and 22 (Fig. 2).

In agreement with the study by Phillips and Muan [10] the diagram specifies incongruent melting of pure $CaFe_2O_4$ at 1216 °C yielding a melt and small amount of $Ca_2Fe_2O_5$. Decreasing of the $CaFe_2O_4$ content brings about an increase of the solidus temperature. The course of the solidus line, which is marked by the dashed line, was determined on the basis of two experimental points.

The findings obtained by the study of phase equilibria in the system $CaCr_2O_4$—$CaFe_2O_4$ provide information on the behaviour of the system in air atmosphere.

From the standpoint of utilization of refractories containing $CaCr_2O_4$ as lining for plant used in the processing of liquid stell, the data on mutual solubility of $CaCr_2O_4$ and $CaFe_2O_4$ contained in slag, occurence of the liquid phase and the modification transformation of β to α $CaCr_2O_4$, involving a change in volume, are of considerable significance. In these plants the linings are likewise exposed to the effect of atmo-
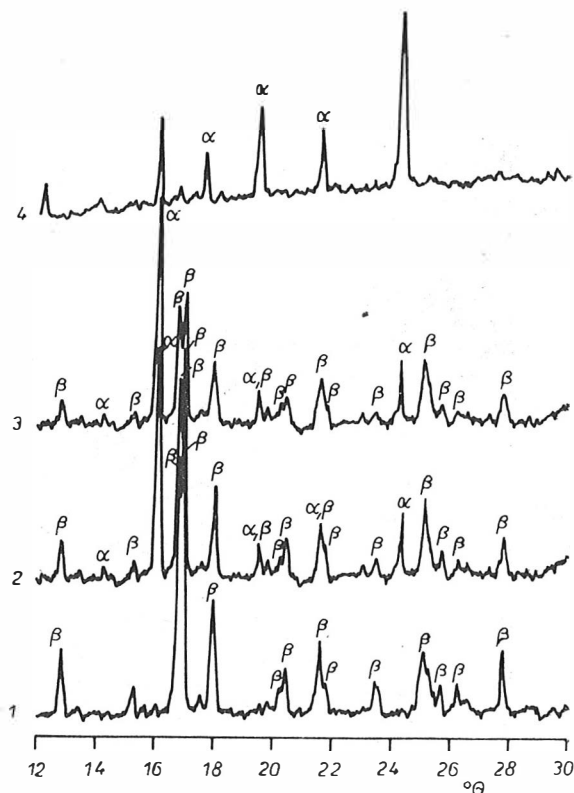

Fig. 2. *Diffractograms of samples 18, 20, 21 and 22; 1 — t = 1780°C, 10 mole % $CaFe_2O_4$, 2 — t = = 1810 °C, 10 mole % $CaFe_2O_4$, 3 — t = 1830 °C, 5 mole % $CaFe_2O_4$, 4 — t = 1830 °C, 3 mole % $CaFe_2O_4$.*

sphere with a partial pressure of oxygen amounting to about 10^{-5} Pa, and this is why the system $CaO—Cr_2O_3—Fe_2O_3$ should be studied in the region of lower partial pressures of oxygen.

CONCLUSION

The system $CaCr_2O_4—CaFe_2O_4$ was studied in the temperature interval of 1280 to 1830 °C. The samples were heated in air atmosphere and the phase diagram constructed on the basis of results of X-ray and microscopical analysis indicates that substitution of Fe^{3+} ions for Cr^{3+} ions in the structure of β-$CaCr_2O_4$ brings about an increase in the temperature of modification transformation. A peritectic temperature of

18

$1830 \pm 10\,°C$ was established. The solubility of $CaFe_2O_4$ in α-$CaCr_2O_4$ at peritectic temperature amounts to about 5 mole %. In the subsolidus region of the system there exists a field of coexistence of α with β $Ca(Cr, Fe)_2O_4$. In the section of the diagram with a higher $CaFe_2O_4$ content the solidus line was established and the probable course of the liquidus line was determined on the basis of two experimental points.

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FÁZOVÉ ROVNOVÁHY V SÚSTAVE CaCr₂O₄—CaFe₂O₄

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Študovala sa sústava CaCr₂O₄—CaFe₂O₄ v teplotnom intervale 1280 až 1830 °C vo vzdušnej atmosfére. Pri príprave vzoriek CaCr₂O₄ s 3 až 90 mol. % CaFe₂O₄ sa vychádzalo z roztokov dusičnanu vápenatého, dusičnanu železitého a dvojchromanu amonného. Po predžíhaní sa tabletky zahrievali po dobu 4 hodín v peci s molybdénovým vinutím v ochrannej atmosfére, resp. vo vysokoteplotnej peci CENTORR typ 10-2068. Teplota sa merala termočlánkami PtRh 18 a Ir-IrRh. Po náhlom ochladení sa vykonala rtg. fázová analýza, mikroskopická analýza a analýza pomocou mikroanalyzátora JXA-5A. Výsledky experimentov, na základe ktorých sa spresnil pseudobinárny diagram pre $p_{O_2} = 0,021$ MPa uvedený na obr. 1, sú zhrnuté v tabuľke I. Z diagramu vyplýva, že náhradou Fe^{3+} iónov za Cr^{3+} ióny v štruktúre CaCr₂O₄ dochádza k zvýšeniu teploty modifikačnej premeny z 1720 na 1830 °C pri obsahu cca 14 mol. % CaFe₂O₄. Rozpustnosť CaFe₂O₄ v α-CaCr₂O₄ pri peritektickej teplote je cca 5 mol. % (viď obr. 2). V časti diagramu s vyšším obsahom CaFe₂O₄ sa stanovila čiara solidus a na základe dvoch experimentálne získaných údajov sa určil pravdepodobný priebeh čiary liquidus.

Obr. 1. Fázový diagram sústavy CaCr₂O₄—CaFe₂O₄ ;
    ● — β-Ca(Cr, Fe)₂O₄, ◑ — β-Ca(Cr, Fe)₂O₄ a tavenina,
    ○ — *tavenina*, ◪ — α-Ca(Cr, Fe)₂O₄ a β-Ca(Cr, Fe)₂O₄,
    □ — α-Ca(Cr, Fe)₂O₄, β-Ca(Cr, Fe)₂O₄ a tavenina,
    ■ — α-Ca(Cr, Fe)₂O₄.
Obr. 2. Difraktogramy vzoriek 18, 20, 21 a 22;
    1 — t = 1780 °C, 10 mol. % CaFe₂O₄,
    2 — t = 1810 °C, 10 mol. % CaFe₂O₄,
    3 — t = 1830 °C, 5 mol. % CaFe₂O₄,
    4 — t = 1830 °C, 3 mol. % CaFe₂O₄.

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ФАЗОВЫЕ РАВНОВЕСИЯ В СИСТЕМЕ $CaCr_2O_4$—$CaFe_2O_4$

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Исследовали систему $CaCr_2O_4$ в температурном интервале 1280—1830 °C в атмосфере воздуха. При получении проб $CaCr_2O_4$ с 3—90 мол. % $CaFe_2O_4$ пользовались растворами нитрата кальция, нитрата трехвалентного железа и бихромата аммония. После предварительного обжига таблетки нагревали 4 часа в печи с молибденовой обмоткой в защитной атмосфере или в высокотемпературной печи CENTORR типа 10-2068. Температуру измеряли с помощью термоэлементов PtRh 18 и Ir — IrRh. После резкого охлаждения проводили рентгеновский фазовый анализ, микроскопический анализ и анализ с помощью микроанализатора JXA—5A. Результаты экспериментов, на основании которых уточняли псевдобинарную диаграмму для $p_{O_2} = 0,021$ МПа, приводимую на рис. 1, имеются в таблице 1. Из диаграммы следует, что заменой ионов Cr^{3+} ионами Fe^{3+} в структуре $CaCr_2O_4$ вызывается повышение температуры полиморфного превращения с 1720 до 1830 °C при содержании приблизительно 14 мол. % $CaFe_2O_4$. Растворимость $CaFe_2O_4$ в α-$CaCr_2O_4$ при перитектической температуре составляет около 5 мол. % (см. рис. 2). В части диаграммы с большим содержанием $CaFe_2O_4$ установили кривую солидуса и на основании двух экспериментально полученных данных установили предполагаемый ход кривой ликвидуса.

Рис. 1. *Фазовая диаграмма* $CaCr_2O_4$—$CaFe_2O_4$; ● — β'-$Ca(Cr, Fe)_2O_4$, ◑ — β-$Ca(Cr, Fe)_2O_4$ *и расплав,*
○ — *расплав,* ◩ — α-$Ca(Cr, Fe)_2O_4$ *и* β-$Ca(Cr, Fe)_2O_4$,
□ — α-$Ca(Cr, Fe)_2O_4$, β-$Ca(Cr, Fe)_2O_4$ *и расплав,*
■ — α-$Ca(Cr, Fe)_2O_4$.

Рис. 2. *Дифракционная картина проб 18, 20, 21 и 22;* 1 — t = 1780 °C, 10 мол. % $CaFe_2O_4$, 2 — t = 1810 °C, 10 мол. % $CaFe_2O_4$, 3 — t = 1830 °C, 5 мол. % $CaFe_2O_4$, 4 — t = 1830 °C, 3 мол. % $CaFe_2O_4$.