ilikáty XXIV, s. 1—6 (1980)

THE EFFECT OF PARTIAL OXYGEN PRESSURE ON THE TEMPERATURE OF β TO α CALCIUM CHROMITE TRANSFORMATION

JAROMÍR HAVLICA, ZDENĚK PÁNEK

Institute of Inorganic Chemistry, Slovak Academy of Sciences 809 34 Bratislava, Dúbravská cesta 5

Received 28. 6. 1978

The temperature of modification transformation of β to α calcium chromite was studied in air atmosphere, in argon and in a $CO—CO_2$ *mixture. It was found that in air the modification transformation takes place at 1720 °C and that the transformation temperature* T_p *decreases with decreasing partial pressure of oxygen in the gaseous phase according to the relationship*

$$T_p = \frac{6.28 \times 10^5}{319.4 - \log p_{O_2}} \quad (T_p\ [K],\ p_{O_2}\ Pa]).$$

A comparison of the data obtained with previous results has shown that when the partial pressure of oxygen is reduced the minimum transformation temperature is 1645 °C. Below this temperature and at lower partial pressures of oxygen β-calcium chromite is reduced and chromium metal is separated.

INTRODUCTION

In connection with increasing demand for materials resisting high temperatures and corrosive environments new compounds with high melting temperatures and suitable physical and chemical properties are sought. Ceramic materials frequently comply with these requirements. One such compound is calcium chromite $CaCr_2O_4$ whose melting temperature of 2170 °C [1] and high chemical resistance render its application promising for instance in iron metallurgy. Apart from theoretical studies on the subject there are patents [2], [3], [4] suggesting the use of alpha calcium chromite based materials for the casting of refractory stones exhibiting outstanding thermomechanical properties.

Determination of the effect of oxygen partial pressure on the temperature at which β-calcium chromite is transformed to the α form is a continuation of a study of its physical-chemical properties of this compound and is aimed at elucidating some problems involved in its practical utilization. Paper [5] was concerned with determining the temperature dependence of the standard Gibbs energy of calcium chromite and showed that when partial pressure of oxygen is reduced below 10^{-10} Pa beta modification is transformed to the alpha form already at temperatures of about 1645 °C.

Both modifications are known and their crystallographic data have been published. The structure of the high-temperature alpha modification was studied by Pausch and Müller—Buschbaum [6] and the low-temperature beta form was dealt with by the work of Hill, Peiser and Rait [7]. The data established in these studies together with the density values are listed in Table I.

The density values indicate that in connection with the structural reconstruction during modification transformation there arise significant volume changes. There is the interesting difference in the distances Ca—O and Cr—O in both modifications which are reported in references [6] and [7]. The mean distance of the calcium ion from the oxygen one calculated on the basis of data given in ref. [6] and [7] has been

Table I

Crystallographic data on alpha and beta modifications of calcium chromite [6], [7]

Modification	Symmetry	Space Group	Elementary cell dimensions (pm)			Density g . cm^{-3}
			a	*b*	*c*	
alpha	ortho-rhombic	Pmmn	1106	584	511	4.24
beta	ortho-rhombic	Pnam	907	1061	299	4.80

changed from 242 pm to 238 pm due to beta-alpha transformation and the Cr—O distance decreased from 203 pm to 201 pm. According to ref. [6] and [7] the beta-alpha transformation results in a decrease in density and the formation of a less dense structure while the mean distances Ca—O and Cr—O decreased. In the case of calcium the beta-alpha transformation resulted in a change in the co-ordination number from 8 to 6 and with chromium the number of closest neighbours is not changed.

Determination of the transformation temperature was dealt with by several authors and their results show considerable differences. For instance, Ford and White [8] established a transformation temperature of 1900 °C. Olshanskij, Cvetkov and Shlepov [9] studied the system CaO—Cr_2O_3 under conditions ruling out oxidation and reported the T_p value of 1570 °C. The effect of partial pressure of oxygen was pointed out in the study by Pánek and Kanclíř [10] who found that in air transformation takes place at 1695 °C and in argon atmosphere already at 1645 °C. The present study was to contribute to the verification or determination of the correct value of modification transformation in air and to evaluate the effect of partial oxygen pressure.

EXPERIMENTAL AND THE RESULTS

The experiments were carried out in a CENTORR type 10-2068 high-temperature furnace. The temperature was measured by a PtRh 18 thermocouple placed in an Al_2O_3 cell. The thermocouple in the cell was calibrated at the melting temperatures of gold, palladium and platinum with an accuracy of ± 5 °C. In the temperature region of about 1700 °C the homogeneous temperature field was about 8 cm in length. The measurements were carried out in air, in argon and in a CO—CO_2 mixture. The partial pressure of oxygen in argon was measured by means of a probe made of ZrO_2-based ceramics stabilized with approx. 15 mass. % CaO. The probe was placed in the same furnace in the temperature range of 750—1200 °C [11] where an almost purely ionic conductivity of the respective ceramic material was ensured. The temperature difference between the platinum electrodes on the solid electrolyte was lower than 5 °C. The concentration gradient in the furnace in its axial direction was not significant. The temperature at the solid electrolyte was measured by a Pt—PtRh 10 % thermocouple placed inside the measuring cell. Air was used as the reference gas.

For the low values of partial oxygen pressures use was made of a mixture of carbon dioxide with carbon monoxide of a known ratio while the mixing of gases was carried out by the procedure described in ref. [5] and p_{O_2} values were calculated by means of the tabullar data in [12].

The samples, crystals of β-calcium chromite several millimeters in length and

10—100 μm in thickness were prepared by crystallization from $CaO—Cr_2O_3—CrO_3$ melt in air atmosphere in the temperature interval of 1250—1100 °C [13]. The samples were heated in platinum crucibles (in molybdenum crucibles in the case of the $CO—CO_2$ gaseous mixture) and the time of firing was in the range of 2—4 hours. After rapid quenching the samples were analysed by optical microscopy and X-ray phase analysis.

The results of the measurements are listed in Table II. It was found that in air atmosphere the transformation of β—α calcium chromite takes place at 1720 °C and as indicated by the diagram in Fig. 1, the temperature of modification transformation T_p decreases with decreasing partial oxygen pressure, which may be expressed by the approximate equation

$$T_p = \frac{6.28 \times 10^5}{3.19 \times 10^2 - \log p_{O_2}} \quad (T_p\,[K], p_{O_2}\,[Pa]). \qquad (1)$$

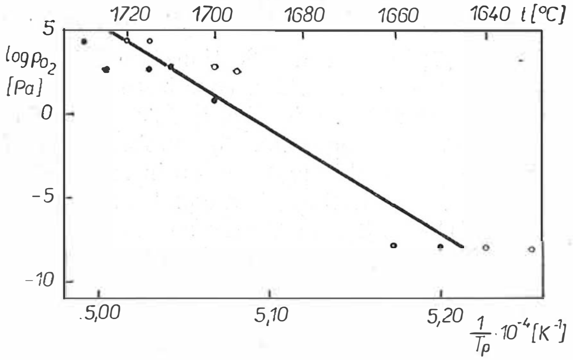

Fig. 1. The temperature of modification transformation vs. partial pressure of oxygen; ○ — content of alpha modification, ● — content of pure beta modification.

Table II

Experiment No	Temperature °C	Time of firing hrs.	log p_{O_2} Pa	The phases present	Notice
1	1730	3	4.32	α, β	air
2	1720	2	4.32	β	air
3	1715	2	4.32	β	air
4	1725	3	2.63	α, β	argon
5	1715	3	2.62	α, β	argon
6	1710	3	2.78	α, β	argon
7	1700	2	2.76	β	argon
8	1695	3	2.51	β	argon
9	1700	3	2.69	β	argon
10	1700	3	0.78	α, β	argon
11	1660	4	—7.82	α, β	$CO—CO_2$
12	1650	2	—7.92	α, β	$CO—CO_2$
13	1640	2	—8.04	β	$CO—CO_2$
14	1630	2	—8.16	β	$CO—CO_2$

DISCUSSION OF THE RESULTS

In the system Ca—Cr—O at a chosen temperature the equilibrium composition is given by partial pressure of oxygen. In our case a decrease in partial pressure of oxygen brings about a decrease in the temperature of the modification transformation. The Gibbs phase rule indicates that if the transformation temperature depends on oxygen content in the gaseous phase the composition of the solid phase must also be subject to a change. At higher temperature one may assume formation of non-stoichiometric calcium chromite with a defective structure and higher partial pressures of oxygen can bring about partial oxidation of chromium, for instance according to the schematic equation

$$Cr^{3+} \longrightarrow Cr^{6+} + 3\,\bar{e}. \tag{2}$$

Hexavalent chromium may escape as chromic trioxide in the form of gas and may be retained in the original structure at the points of Cr^{3+} producing an equal number of vacancies which compensate the positive charge increment

$$CaCr_2O_4 + 3/2\,O_2 \longrightarrow CrO_3 + CaV_{Cr}Cr_{Cr}O_4. \tag{3}$$

According to ref. [6] and [7] in both modifications the Cr^{3+} ions are surrounded in the structure by six oxygen atoms which constitute octahedrons. During the β—α transformation the Cr—O distance is slightly increased. If calcium chromite behaves according to the schematic equation (3) the formation of vacancies with an effective charge of 3— will probably result in an increase in the volume of the respective octahedron and even formation of an equal number of Cr^{6+} ions of diameters smaller than those of Cr^{3+} will probably not permit an approach which would compensate the increment in volume. The larger Cr—O distances abide better with the beta-form, which may be the reason why the beta modification survives in the higher temperature regions.

One cannot rule out the possibility that the Cr^{6+} ions were present already in the structure of the original calcium chromite. The samples were prepared in air by crystallization from a melt containing Cr^{6+} ions and the monocrystals may be assumed to have been saturated with this component already during their preparation.

The hypothesis according to which the β — α transformation is affected by oxidation and formation of a gaseous phase can be proved correct by the kinetics of the respective process which was studied on a dilatometer within the present study. The experiments have shown that in air atmosphere the transformation was substantially faster than in argon. In the experiments the amounts of vapourized chromic trioxide were not assumed to be large enough for influencing the phase composition of the samples being studied.

Our experiments have further shown that in the case of reducing partial pressure of oxygen, 1645 °C is the lowest equilibrium temperature at which α-modification is capable of existing. According to the results of work [5] calcium chromite is decomposed at lower temperatures and at lower partial oxygen pressures according to the equation

$$2\,CaCr_2O_4 \longrightarrow 2CaO + 4\,Cr + 3\,O_2. \tag{4}$$

The results obtained are in a satisfactory agreement with the data obtained earlier by the present authors [10]. The modification transformation temperature $T_p = 1570$ °C established in study [9] is not in line with our results. On the other hand, in the case of the value found by Ford and White [8], $T_p = 1900$ °C, it may be assumed that the stabilization of the low-temperature form was due for instance to the formation of calcium vacancies during formation of Cr_2O_3 solid solutions in $CaCr_2O_4$. For the purpose of elucidating this problem the present authors have carried out orientation experiments with the aim of determining the modification transformation temperature of calcium chromite containing an addition of Cr_2O_3. It was found that in air atmosphere no modification transformation takes place at temperatures of up to 1780 °C.

CONCLUSION

It was found that β-calcium chromite is transformed to its α-form in air atmosphere at 1720 °C and that the temperature decreases with decreasing partial oxygen pressure according to relationship (1). A comparison of the results obtained with those of study [5] showed that when partial pressure of oxygen is reduced the minimum transformation temperature is 1645 °C. Below this temperature at partial oxygen pressures lower than 10^{-10}. Pa, β-calcium chromite is reduced and chromium metal is separated.

References

[1] Wartenberg H., Reusch H. J., Saran E.; J. Anorg. Chem. *230*, 257 (1937).
[2] Patent 74 69 713, Japan Kokai.
[3] Patent 74 69 714, Japan Kokai.
[4] Patent 74 69 715, Japan Kokai.
[5] Havlica J., Pánek Z.: Silikáty *21*, 1, 13 (1977).
[6] Pausch H., Müller—Buschbaum Hk.: Z. Anorg. Allg. Chem. *405*, 113 (1974).
[7] Hill P. M., Peiser H. S., Rait J. R.: Acta Cryst. *9*, 981 (1956).
[8] Ford W. F., White J.: Trans. Brit. Ceram. Soc. *48*, 291 (1949).
[9] Olshanskij J. I., Cvetkov A. I., Shlepov V. K.: Dokl. AN SSSR *96*, 5, 1007 (1954).
[10] Pánek Z., Kanclíř E.: Silikáty *20*, 2, 113 (1976).
[11] Taylor R. W., Schmalzried H.: J. Phys. Chem. *68*, 9. 2444 (1964).
[12] Barin I., Knacke I.: *Thermochemical Properties of Inorganic Substances.* Springer-Verlag, Berlin—Heidelberg—New York 1973.
[13] Figusch V., Pánek Z. in: *Thermodynamics and Properties of Condesed Silicate and Oxidic Systems* (in Russian), (Ed. Kanclíř E., Pánek Z.) p. 182. Veda, Bratislava 1976.

VPLYV PARCIÁLNEHO TLAKU KYSLÍKA NA TEPLOTU MODIFIKAČNEJ PREMENY $\beta—\alpha$ KALCIUMCHROMITU

Jaromír Havlica, Zdeněk Pánek

Ústav anorganickej chémie SAV, Bratislava

Sledovala sa teplota modifikačnej premeny $\beta—\alpha$ kalciumchromitu vo vzdušnej atmosfére, v argóne a v zmesi tvorenej kysličníkom uhoľnatým a kysličníkom uhličitým. Mnohokryštály β-kalciumchromítu o dĺžke niekoľkých milimetrov a hrúbke 10—100 μm sa temperovali v platinových a v prípade zmesi $CO—CO_2$ v molybdénových téglikoch. Obsah kyslíka v argóne sa meral pomocou kyvety zhotovenej z ZrO_2, stabilizovaného cca 15-mi hmot. % CaO, ktorá bola umiestnená priamo v pracovnom priestore v intervale teplôt 800 až 1200 °C. Rovnovážny parciálny tlak kyslíka v zmesi $CO—CO_2$ sa vypočítal na základe zmiešavacieho pomeru plynov a tabelárnych údajov [12]. Získané výsledky sú uvedené v tabuľke II a v grafickej závislosti na obr. 1. Zistilo sa, že teplota modifikačnej premeny T_p $\beta—\alpha$ kalciumchromitu vo vzdušnom prostredí je 1720 °C a klesá so znižujúcím sa parciálnym tlakom kyslíka podľa vzťahu

$$T_p = \frac{6{,}28 \cdot 10^5}{319{,}4 - \log p_{O_2}} \quad (T_p\,[K],\, p_{O_2}\,[Pa]).$$

Pokles teploty modifikačnej premeny, ku ktorému dochádza s poklesom parciálneho tlaku kyslíka v plynnej fáze, sa vysvetľuje tvorbou nestechiometrického kalciumchromitu a vznikom poruchovej štruktúry.

Obr. 1. Závislosť teploty modifikačnej premeny od parciálneho tlaku kyslíka;
● — výskyt alfa modifikácie, ○ — výskyt čistej beta modifikácie.

ВЛИЯНИЕ ПАРЦИАЛЬНОГО ДАВЛЕНИЯ КИСЛОРОДА НА ТЕМПЕРАТУРУ ПОЛИМОРФНОГО ПРЕВРАЩЕНИЯ β — α ХРОМИТА КАЛЬЦИЯ

Яромир Гавлица, Зденек Панек

Институт неорганической химии САН, Братислава

Исследовали температуру полиморфного превращения β—α хромита кальция в воздушной среде, в аргоне и в смеси, состоящей из окиси и двуокиси углерода. Монокристаллы β-хромита кальция длиной в несколько милиметров и толщиной в 10 —100 μм темперировали в платиновых тиглях, и в случае смеси $CO—CO_2$ в молибденовых тиглях. Содержание кислорода в аргоне измеряли с помощью кюветки, изготовленной из ZrO_2, стабилизированной приблизительно 15 % CaO, которую поместили непосредственно в рабочее пространство в интервале температур 800—1200 °C. Равновесное парциальное давление кислорода в смеси $CO—CO_2$ расчитали на основании отношения смешивания газов и табулярных данных [12]. Полученные результаты приводятся в таблице II и в виде графической зависимости на рис. 1. Было установлено, что температура полиморфного превращения T_p β—α хромита кальция в воздушной среде составляет 1720 °C и понижается с парциальным давлением кислорода согласно отношению:

$$T_p = \frac{6{,}28 \,.\, 10^5}{319{,}4 - \log p_{O_2}} \quad (T[\mathrm{K}]\,.\,p_{O_2}[\mathrm{Pa}]).$$

Понижение температуры полиморфного превращения, проходящее с понижением парциального давления кислорода в газовой фазе, объясняется образованием нестехиометрического хромита кальция и образованием дефектной структуры.

Рис. 1. Зависимость температуры полиморфного превращения от парциального давления кислорода; ● — появления α-модификации, ○ — появление чистой β-модофикации.