Silikáty XXV, s. 169—171 (1981)

PHASE EQUILIBRIA IN THE SYSTEM Ca—Cr—O

ZDENĚK PÁNEK

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

Received 24. 4. 1980

The disagreement between the rates of shrinkage of powdered pressed specimens of the given system during their sintering, and the reactions specified in the equilibrium phase diagram necessitated its revision in the concentration region of 0—50 wt. % Cr_2O_3. $Ca_3(CrO_4)_2$ *was found to melt incongruently at 1255 ± ± 5 °C producing* $Ca_5(CrO_4)_3$ *and a melt.* $Ca_5(CrO_4)_3$ *likewise melts incongruently producing* CaO *and melts at 1275 ± 5 ° C. An equilibrial phase diagram taking into account these new findings has been constructed.*

INTRODUCTION

The original phase diagram of the system Ca—Cr—O expressing the phase conditions in air atmosphere [1] specifies a congruent melting of the compound $Ca_3(CrO_4)_2$ at 1228 °C and the solidus temperature in the concentration range between CaO and this compound at 1174 °C. A previous paper by the present authors [3] was concerned above all with the subsolidus region in the concentration range of 40—80 wt. % Cr_2O_3.

When compacted powders of the system CaO—Cr_2O_3 or CaO—MgO—Cr_2O_3 were sintered in air in the region of high CaO concentrations with Cr_2O_3 contents up to 20 wt. %, there always appeared two peaks on the shrinkage rate curves, namely one at 1080—1120 °C (less distinct) and the other at 1280—1300 °C (the main one). These peaks could not be explained on the basis of reactions following from the diagrams in literature [1]—[3] so that this diagram required a revision within the concentration range of 0—50 wt. % Cr_2O_3.

CONSTRUCTION OF THE PHASE DIAGRAM

The data necessary for the construction of the equilibrium phase diagram, that is temperatures and phase compositions corresponding to the known chemical composition in air atmosphere ($P_{H_2O} \doteq 1.8$ kPa) were obtained by the abrupt quenching method followed by X-ray and microscopic phase analysis. Incongruent melting of $Ca_3(CrO_4)_2$ was found to take place at 1255 ± 5 °C producing $Ca_5(CrO_4)_3$ [4] and a melt. At 1275 ± 5 °C the compound $Ca_5(CrO_4)_3$ melts incongruently producing CaO and a melt. The incongruent melting of the compounds has likewise been confirmed by means of DTA, and in the case of $Ca_3(CrO_4)_2$ additionally by determining the cooling curve [5]. The pseudobinary equilibrium phase diagram constructed on the basis of newly established data as well as on that of published ones [1—3] is shown in Fig. 1.

CONCLUSION

Having found that the compound $Ca_3(CrO_4)_2$ melts incongruently producing $Ca_5(CrO_4)_3$ and a melt, in contrast to the congruent melting described so far in lite-

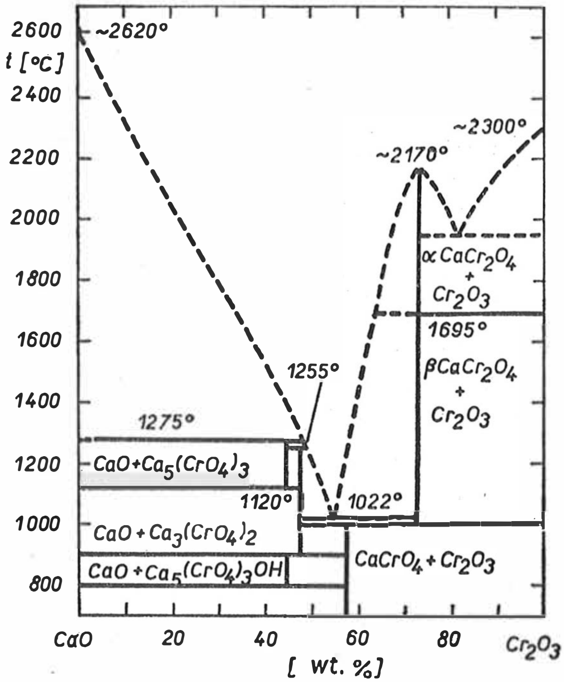

Fig. 1. Pseudobinary equilibrium phase diagram of the system Ca—Cr—O *in air atmosphere* (p_{H_2O} ≐ 1.8 kPa).

rature, the author revised the existing phase diagram [1] in the concentration range of 0—50 wt. % Cr_2O_3. The solidus temperatures were determined together with the range of co-existing phases in the subsolidus region, as well as the liquidus curve in the temperature range of 1200—1350 °C.

References

[1] Ford W. F., Rees W. J.: Trans. Brit. Ceram. Soc. *48*, 291 (1949).
[2] Muan A., Osborn E. F.: *Phase Equilibria Among Oxides in Steelmaking*, p. 83. Addison-Wesley Publishing Company, Inc., Reading, Massachussetts 1965.
[3] Pánek Z., Kanclíř E.: Silikáty *20*, 113 (1976).
[4] Figusch V., Pánek Z.: Synthesis of $Ca_5(CrO_4)_3$ (to be published).
[5] Daněk V., Ličko T.: Research Report ŠPZV IV-5-1/1, Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava (1979).

ФАЗОВЫЕ РАВНОВЕСИЯ В СИСТЕМЕ Ca—Cr—O

Зденек Панек

Институт неорганической химии Словацкой академии наук, Братислава

Пересматривали псевдобинарную равновесную диаграмму системы Ca—Cr—O [1—3] в концентрационной области 0—50 % по весу Cr_2O_3 в атмосфере воздуха. Был доказан инконгруентный способ плавления (до сих пор приводился конгруентный способ плавле-

ния) с образованием $Ca_5(CrO_4)_3$ и расплава при температуре 1255 + 5 °C. Соединение $Ca_5(CrO_4)_3$ плавится также инконгруентно с образованием CaO и расплава при температуре 1275 + 5 °C. На основании уже известных и вновь полученных данных собрали псевдобинарную фазовую диаграмму, которая приводится на рис. 1.

Рис. 1. Псевдобинарная равновесная фазовая диаграмма системы Ca—Cr—O *в атмосфере воздуха* (p_{H_2O} = 1,8 кПа).

FÁZOVÉ ROVNOVÁHY V SÚSTAVE Ca—Cr—O

Zdeněk Pánek

Ústav anorganickej chémie SAV, Bratislava

Revidoval sa pseudobinárny rovnovážny fázový diagram sústavy Ca—Cr—O [1—3] v koncentračnej oblasti 0—50 % hmot. Cr_2O_3 vo vzdušnej atmosfére. Dokázal sa inkongruentný spôsob topenia (doposiaľ sa uvádzal kongruentný spôsob topenia) zlúčeniny $Ca_3(CrO_4)_2$ za vzniku $Ca_5(CrO_4)_3$ a taveniny pri teplote 1255 ± 5 °C. Zlúčenina $Ca_5(CrO_4)_3$ sa topí tiež inkongruentne za tvorby CaO a taveniny pri teplote 1275 ± 5 °C. Na základe známych a novozískaných údajov zkonštruoval sa pseudobinárny rovnovážny fázový diagram, ktorý sa uvádza na obr. 1.

Obr. 1. Pseudobinárny rovnovážny fázový diagram sústavy Ca—Cr—O *vo vzdušnej atmosfére* (p_{H_2O} ≐ 1,8 kPa).