

A RE-EXAMINATION OF THE SYSTEM CaO-TiO_2 AT LIQUIDUS TEMPERATURES*

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SUMMARY

The liquidus curve of the system CaO-TiO_2 has been determined by hot-stage microscopy. The shape of the curve on the TiO_2 -rich side of perovskite, CaO.TiO_2 , approximately coincided with that determined by DE VRIES, ROY AND OSBORN, except for a possible slight discontinuity at approximately 1870°C . A significant discontinuity on the CaO -rich side of the perovskite curve was observed at the same temperature level. Its location suggested the existence, at least at high temperatures, of a compound possibly having the composition $4\text{CaO}.3\text{TiO}_2$, and/or that of a transformation to a high-temperature form of perovskite.

The position of the eutectic with CaO and, consequently, that of the CaO curve appeared to be richer in TiO_2 than was indicated by the results of cone-fusion methods used by other investigators.

INTRODUCTION

A re-examination of phase equilibria in the system CaO-TiO_2 was prompted by results of experiments conducted in the system $\text{CaO-Nb}_2\text{O}_5\text{-TiO}_2$. Phase equilibrium relationships in the system $\text{CaO-Nb}_2\text{O}_5\text{-TiO}_2$ were studied, in the first instance, with a Griffin-Telin hot-stage microscope¹ equipped with a Pt/5%Rh vs. Pt/20%Rh thermocouple for the determination of the liquidus temperatures. The opacity of the melts and the high liquidus temperatures that are involved in the part of the $\text{CaO-Nb}_2\text{O}_5\text{-TiO}_2$ system near the CaO-TiO_2 binary prevented observations of phenomena in the melt being made with that instrument.

However, when the instrument was equipped with an Ir vs. 60% Ir/40%Rh thermocouple², not only could temperatures up to 2140°C be reached, but also the opacity of the melts decreased to such an extent that the determination of liquidus temperatures in the high-lime part of the $\text{CaO-Nb}_2\text{O}_5\text{-TiO}_2$ system could be extended to the CaO-TiO_2 binary system.

Phase equilibrium relationships in the system CaO-TiO_2 have been previously studied by COUGHANOUR *et al.*³, and DE VRIES *et al.*⁴. A later study by ROTH⁵ was concerned primarily with the existence of a compound having the composition 4CaO .

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RESULTS AND DISCUSSION

The results of the liquidus determinations in the system CaO-TiO₂ are depicted in Fig. 1 and are listed in Table I. They are compared with the results of DE VRIES *et al.*⁴ and of ROTH⁵ in Fig. 2.

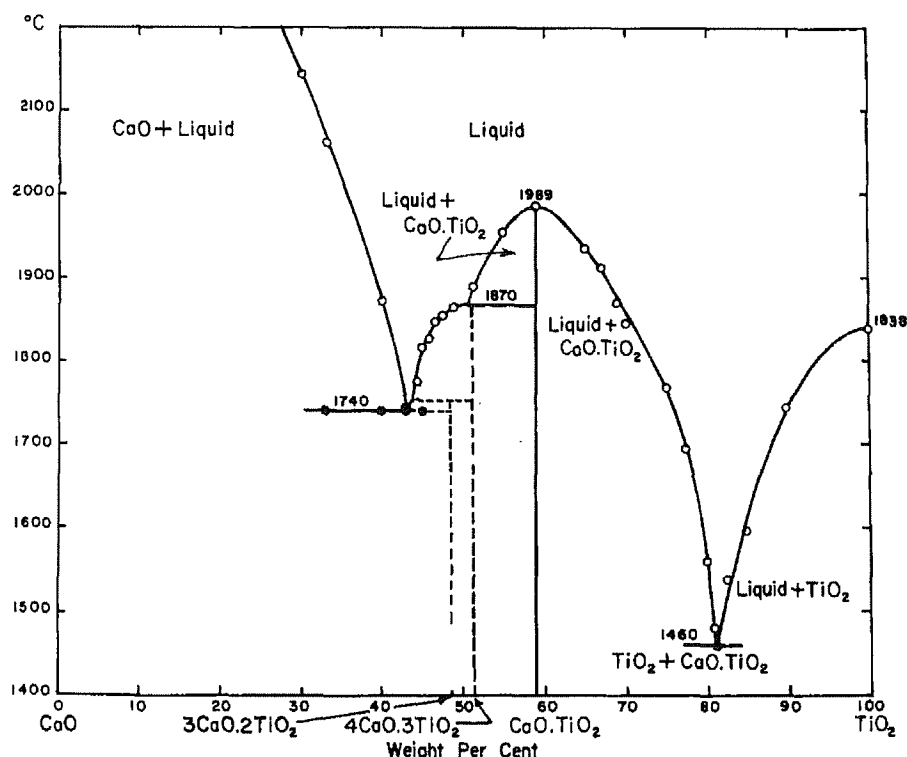


Fig. 1. Results of liquidus determinations of compositions in the CaO-TiO₂ system. (Open circles are hot-stage microscope determinations; filled circles are "strip furnace" determinations.)

The results of the determinations on the TiO₂ side of perovskite (CaO.TiO₂) appear to coincide essentially with those obtained by DE VRIES *et al.*⁴, except for a possible slight discontinuity near 1870°C.

The position of the eutectic at 81.5% TiO₂ coincides approximately with that given by other workers, and the temperature of 1460°C is the same as that determined by DE VRIES *et al.* The shape of the liquidus of the TiO₂ field is slightly steeper in our measurements than in those of the other diagrams, and the melting temperature of TiO₂ of 1838°C coincided with that of ROTH⁵ (1840°C). Thus, on the whole, no major differences were indicated in the TiO₂-rich side of the diagram.

The liquidus of the CaO field in our study, however, has a position notably different from the other diagrams. It ascends steeply from a eutectic at 43% TiO₂ and 1740°C. The differences in the results are very probably to be attributed to the disadvantages of the cone-fusion method used by the other investigators, since it prevents the observation of a relatively small quantity of crystals in a melt. When a cone has completely collapsed and forms a puddle, crystals may still be present at higher temperatures when the liquidus is steep. This possibility has been mentioned by DE VRIES, *et al.*⁴ in discussing the results of their own work.

The small quantity of crystals that could be expected to be present in the melt

when the liquidus is steep can, however, be observed with the hot-stage microscope. In addition, CaO developed typical dendritic crystals that floated on the melt and, because of their transparency, were difficult to observe, even with the hot-stage microscope. No explanation can be given for the difference in the eutectic temperatures—DE VRIES *et al.*⁴: $1695 \pm 5^\circ\text{C}$, ROTH⁵: 1725°C , while no evidence of liquid could be detected below $1740 \pm 10^\circ\text{C}$ in the present study. The cone-softening temperature measurement of the eutectic was calibrated with gehlenite and α -Ta₂O₅, having melting points of 1590°C and 1872°C , respectively.

The melting point of perovskite (1989°C) determined in the present study was higher than 1970°C reported by DE VRIES *et al.*⁴. However, when the experimental errors in both methods are taken into account, this difference is probably not significant.

Probably the most significant deviation from the previously-reported curves is that the CaO-rich side of the perovskite curve did not appear to be smooth. A significant discontinuity appeared to be present in between the compositions of 4CaO.3TiO₂ and 3CaO.2TiO₂. This discontinuity extended into the CaO-Nb₂O₅-TiO₂ system, forming in it a definite boundary between two fields. The results of the work on the CaO-Nb₂O₅-TiO₂ system will be reported in the near future, and will illustrate this point.

The problem concerning the existence of the phases 3CaO.2TiO₂ and 4CaO.3TiO₂ has been studied extensively by IMLACH AND GLASSER⁶. Their tentative conclusion was that no phases exist having compositions lying between 3CaO.2TiO₂ and CaO.TiO₂, at least within the temperature range over which their experiments were done. This limitation made by them in their discussion must, apparently, be significant in view of the results obtained in the present study. The following is submitted as a contribution to the problem of the composition of the calcium titanates at liquidus temperatures.

The position and shape of the discontinuity in the liquidus curve between the 3CaO.2TiO₂ and 4CaO.3TiO₂ compositions cannot be indicative of the presence of 3CaO.2TiO₂, melting either congruently or incongruently. Consequently, two possibilities are open:

(a) The slight indication of a discontinuity in the TiO₂-rich side of the perovskite curve is significant and the liquidus curves on both sides of CaO.TiO₂ could be considered to be bending for a short distance towards its melting point reported by ROTH⁵. These phenomena could be considered as indicative of the presence of a transformation in perovskite at high temperatures and may account for the difference between the melting points of CaO.TiO₂ reported by DE VRIES *et al.*⁴ and by ROTH⁵. IMLACH AND GLASSER⁶ assumed that the transformation of orthorhombic into cubic perovskite takes place at about 1260°C according to the results of the experiments done by NAYLOR AND COOK⁷, so that a high-temperature transformation of perovskite could then involve only *two* cubic modifications.

Since the melting phenomena on the TiO₂ side of the curve were particularly difficult to observe, the presence of the discontinuity on that side remains uncertain when the results of the liquidus determinations only along the CaO.TiO₂ binary are considered. Some evidence, however, was obtained in studies in the CaO-Nb₂O₅-TiO₂ system that there is a possibility of a transformation occurring in perovskite at approximately 1870°C , in addition to the presence of both 4CaO.3TiO₂ and 3CaO.2TiO₂.

It is proposed by the present authors that the variations are partly due to quench effects. When compositions that do not develop glasses are quenched, results from these quenches cannot be considered to be necessarily representative of the conditions from which the quenches were made. The formation of phases having crystal structures closely resembling each other in a range limited by high temperatures, will necessarily cause the development of structure variations due to strain. It is well-known that the perovskite structure is pseudo-cubic. It is quite possible that the arrangement of the "pseudo-cells" can easily be disturbed to a slight extent and produce superstructures, forming weak lines in the X-ray diffraction powder patterns.

The conclusions concerning the composition of calcium titanates, based on the results of the present study and on the evidence obtained by other investigators are as follows:

(a) The results of the studies by FISK⁹, COUGHANOUR *et al.*³, DE VRIES *et al.*⁴ and by IMLACH AND GLASSER⁶ established the existence, at least at room temperature, of a compound having a composition 3CaO.2TiO₂. This phase is either obtained as an end-product of crystallisation in the 1740°C eutectic with CaO, or as a product of 4CaO.3TiO₂ transforming into 3CaO.2TiO₂ and CaO.TiO₂.

(b) The possibility that a compound exists at high temperatures having the composition 4CaO.3TiO₂ or close to it, should not be rejected without definite evidence of conditions at the temperatures near the liquidus curve. The shape of the liquidus curve determined in the present study would indicate conclusively that a compound having a composition between 3CaO.2TiO₂ and CaO.TiO₂ exists, if it were not for the possible existence of a high-temperature form of CaO.TiO₂. Since this last possibility can be discounted because of the results of the experiments done by NAYLOR AND COOK⁷, the discontinuity in the liquidus curve cannot be explained otherwise than by the existence of the compound, 4CaO.3TiO₂.

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