

## Short Communications

The Phase Diagram (80 %  $\text{TiO}_2$  + 20 %  $\text{Al}_2\text{O}_3$ ) —  $\text{CaF}_2$ 

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According to Ref. 1 the system  $\text{TiO}_2$ — $\text{CaF}_2$  has a eutectic point at  $1360^\circ\text{C}$  corresponding to a composition of 57 %  $\text{TiO}_2$  + 43 %  $\text{CaF}_2$ , and a two-liquid area above a temperature of about  $1365^\circ\text{C}$  and between the compositions 55 %  $\text{TiO}_2$  + 45 %  $\text{CaF}_2$  and 6 %  $\text{TiO}_2$  + 94 %  $\text{CaF}_2$ .

The melting point of  $\text{CaF}_2$  is  $1418^\circ\text{C}$ ,<sup>2</sup> of  $\text{TiO}_2$ ,  $1840^\circ\text{C}$ ,<sup>3</sup> and of  $\text{Al}_2\text{O}_3$ ,  $2040^\circ\text{C}$ .<sup>4</sup>

According to Ref. 5 the system  $\text{Al}_2\text{O}_3$ — $\text{CaF}_2$  has no compounds and no solid solutions but a eutectic point at  $1290^\circ\text{C}$  corresponding to a composition of 9 %  $\text{Al}_2\text{O}_3$  + 91 %  $\text{CaF}_2$ . This is, however, neither in agreement with Ref. 6 that has found solid solutions between  $\text{Al}_2\text{O}_3$  and  $\text{CaF}_2$  but no compounds, nor with Ref. 7 that has found the two compounds  $5\text{Al}_2\text{O}_3\cdot\text{CaF}_2$  and  $\text{Al}_2\text{O}_3\cdot\text{CaF}_2$ .

The system  $\text{TiO}_2$ — $\text{Al}_2\text{O}_3$  has one compound:  $\text{Al}_2\text{O}_3\cdot\text{TiO}_2$ . The eutectic between  $\text{Al}_2\text{O}_3\cdot\text{TiO}_2$  and  $\text{TiO}_2$  lies at  $1705^\circ\text{C}$  corresponding to a composition of 80 %  $\text{TiO}_2$  + 20 %  $\text{Al}_2\text{O}_3$ .<sup>5</sup>

The phase diagram for the system (80 %  $\text{TiO}_2$  + 20 %  $\text{Al}_2\text{O}_3$ )— $\text{CaF}_2$  has now been studied by heat treatment at various temperatures in an atmosphere of pure dry argon, of powder mixtures of compositions ranging from 100 % of (80 %  $\text{TiO}_2$  + 20 %  $\text{Al}_2\text{O}_3$ ) to 100 %  $\text{CaF}_2$  and subsequent cooling of the samples in different ways, usually quenching in  $\text{CCl}_4$  at room temperature. The experiments were performed in a specially constructed apparatus used in a series of phase diagram studies (Refs. 1—13). The raw materials used were of highest

analytical purity. They were dried separately:  $\text{CaF}_2$  at  $800^\circ$ ,  $\text{TiO}_2$  at  $1200^\circ$ , and  $\text{Al}_2\text{O}_3$  ( $\alpha$ ) at  $1200^\circ$  (in order to prevent fluorine losses in the form of HF by reaction of  $\text{CaF}_2$  with water vapor when heat treating the powder mixtures) before the grinding, weighing, and mixing. The powders and mixtures were always stored in desiccators with  $\text{Mg}(\text{ClO}_4)_2$ . Each sample was placed in a small Pt envelope and suspended in the hot zone of a vertical Pt 40 % Rh-wound furnace for a period of 60—120 min.

The flow properties of the sample at the experimental temperature were estimated from the shape of the sample after quenching. One half of each sample was prepared for microscopic examination and the other half was used for obtaining X-ray powder photographs with a Guinier camera. The flow property, the microstructure and the phase analysis were all combined for estimating the position of the liquidus.

The position of all samples will be found in Fig. 1 together with the phase diagram drawn in accordance with the results. The liquidus has a lowest point at  $1280^\circ$  corre-

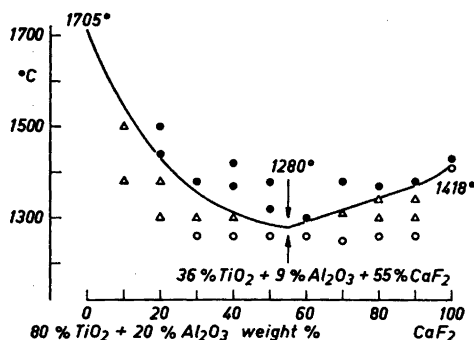


Fig. 1. The phase diagram (80 %  $\text{TiO}_2$  + 20 %  $\text{Al}_2\text{O}_3$ )— $\text{CaF}_2$ .

● fully melted samples;  $\Delta$  partly melted samples;  $\circ$  not melted samples.

sponding to a composition of 36 %  $\text{TiO}_2$  + 9 %  $\text{Al}_2\text{O}_3$  + 55 %  $\text{CaF}_2$ . When fully melted samples of compositions between 80 %  $\text{TiO}_2$  + 20 %  $\text{Al}_2\text{O}_3$  and 36 %  $\text{TiO}_2$  + 9 %  $\text{Al}_2\text{O}_3$  + 55 %  $\text{CaF}_2$  (*i.e.* to the left of the lowest point) were cooled to room temperature, two crystalline phases were formed:  $\text{TiO}_2$  (rutile) and  $\text{CaF}_2$  and a glass-phase. Furthermore two more phases were formed in small amounts, one of them being  $\text{CaO}\cdot\text{TiO}_2$  and the other being an unknown crystalline phase that was here called F10.

When fully melted samples of compositions between 36 %  $\text{TiO}_2$  + 9 %  $\text{Al}_2\text{O}_3$  + 55 %  $\text{CaF}_2$  and 100 %  $\text{CaF}_2$  (*i.e.* to the right of the lowest point) were cooled to room temperature, the two crystalline phases  $\text{CaF}_2$  and  $\text{TiO}_2$  (rutile) were also formed together with a glass-phase. Furthermore the crystalline phase  $\text{CaO}\cdot\text{TiO}_2$  was formed in small amounts.

The amount of glass-phase formed in the two cases varied with the initial composition of the sample. The closer the initial composition was to the composition of the lowest melting point, the larger was the amount of glass formed.

Table 1. *d*-Values of the unknown phase F10.

Lattice distances <i>d</i> in Å units	Relative intensities
8.83	VW
4.958	VW
4.192	W
3.598	W
3.520	W
3.328	VW
2.961	VVW
2.933	W
2.843	VW
2.675	VVW
2.520	VVW
2.485	W
2.002	VW
1.886	W
1.778	VVW
1.593	VW
1.542	VVW

M medium, WM weak medium, W weak, VW very weak, VVW very very weak.

An estimate by quantitative microscopy seemed to indicate that the amount of glass formed in a sample near the composition of the lowest melting point (for instance in the sample with 60 %  $\text{CaF}_2$ ) was about 40–70 %.

Measuring of the *d*-values of the unknown phase (called F10) with the help of the Guinier method and  $\text{CuK}\alpha$  radiation and with  $\text{CaF}_2$  as an internal standard gave the results shown in Table 1.

When fully melted samples of compositions between 36 %  $\text{TiO}_2$  + 9 %  $\text{Al}_2\text{O}_3$  + 55 %  $\text{CaF}_2$  and 100 %  $\text{CaF}_2$  (for instance  $B_1$  or

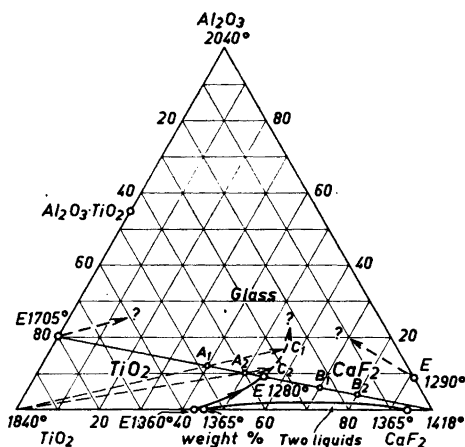


Fig. 2. The formation of glasses in the system  $\text{TiO}_2$ – $\text{Al}_2\text{O}_3$ – $\text{CaF}_2$ .  $\text{TiO}_2$ – $\text{Al}_2\text{O}_3$  according to Ref. 8;  $\text{Al}_2\text{O}_3$ – $\text{CaF}_2$  according to Ref. 5;  $\text{TiO}_2$ – $\text{CaF}_2$  according to Ref. 1; (80 %  $\text{TiO}_2$  + 20 %  $\text{Al}_2\text{O}_3$ )– $\text{CaF}_2$  according to this investigation.

$B_2$  in Fig. 2) are cooled to room temperature, the glass-phase is supposed to form in the following way. When the precipitation of  $\text{CaF}_2$  from the melt is taking place, the composition of the melt approaches that of point E in the section (80 %  $\text{TiO}_2$  + 20 %  $\text{Al}_2\text{O}_3$ )– $\text{CaF}_2$ , *i.e.* the eutectic composition. After that the precipitation continues along the boundary between the crystallization fields for  $\text{TiO}_2$  and  $\text{CaF}_2$ , when the two phases  $\text{TiO}_2$  and  $\text{CaF}_2$  are crystallizing simultaneously. When the melt has reached a composition somewhere in the region 20–40 %  $\text{Al}_2\text{O}_3$  it will form a glass. On the other hand, in

the samples on the other side of the eutectic, *i.e.* with less than 55%  $\text{CaF}_2$ , the formation of glass is first preceded by a precipitation of  $\text{TiO}_2$ . As a consequence the composition of the melt is, *e.g.*, changing from  $A_1$  to  $C_1$  or from  $A_2$  to  $C_2$  according to Fig. 2. When the composition of the melt has reached the boundary between the crystallization fields for  $\text{TiO}_2$  and  $\text{CaF}_2$ , the precipitation continues along that boundary while the two phases  $\text{TiO}_2$  and  $\text{CaF}_2$  are crystallizing simultaneously. The glass formed in samples to the left of the eutectic may thus have the same composition as the glass formed in samples to the right of the eutectic and the exact composition of this glass is not necessarily depending on the initial composition of the melted sample.

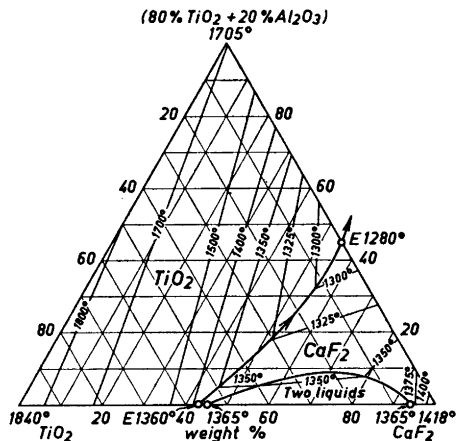


Fig. 3. Tentative phase diagram for the system  $\text{TiO}_2$ -(80%  $\text{TiO}_2$  + 20%  $\text{Al}_2\text{O}_3$ )- $\text{CaF}_2$ .  $\text{TiO}_2$ -(80%  $\text{TiO}_2$  + 20%  $\text{Al}_2\text{O}_3$ ) according to Ref. 8;  $\text{TiO}_2$ - $\text{CaF}_2$  according to Ref. 1; (80%  $\text{TiO}_2$  + 20%  $\text{Al}_2\text{O}_3$ )- $\text{CaF}_2$  according to this investigation.

In combining the results of the present work with those of Refs. 1 and 8 an attempt has been made to construct the ternary phase diagram for the system  $\text{TiO}_2$ -(80%  $\text{TiO}_2$  + 20%  $\text{Al}_2\text{O}_3$ )- $\text{CaF}_2$  (Fig. 3). Nothing is known about the extension of the two-liquid area of the system  $\text{TiO}_2$ - $\text{CaF}_2$  into the ternary system. Thus its extension was drawn tentatively in Fig. 3. The ternary phase diagram  $\text{TiO}_2$ -(80%  $\text{TiO}_2$  + 20%  $\text{Al}_2\text{O}_3$ )- $\text{CaF}_2$  in Fig. 3 shows the

boundary between the primary crystallization fields for  $\text{TiO}_2$  and  $\text{CaF}_2$  and the liquidus isotherms.

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## The Preparation of 1,1-Dichloro-3,3-dibromobutanone-2

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In connection with work on the mechanism of the Favorsky rearrangement, we wished to prepare 1,1-dichloro-3,3-dibromobutanone-2.<sup>1</sup> The common method for the preparation of tetrahaloketones is the acid catalyzed halogenation.<sup>2</sup> However, in the present case, this method seems to be without success. Although 3,3-dibromobutanone-2 can be prepared in good yields by bromination with *N*-bromosuccinimide,<sup>3</sup> it rearranges easily in acid media to the symmetrical 1,3-dibromobutanone-2.<sup>4</sup>