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PHASE EQUILIBRIA IN THE SYSTEMS TiO_2, TiO_2-SiO_2 AND TiO_2-Al_2O_3

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ABSTRACT

The stable form of TiO_2 above 400° C. was found to be rutile with a melting point of 1,825° C. It forms no compounds with SiO_2, but gives a eutectic with 89.5 wt. percent SiO_2 at 1,540° C. With Al_2O_3, a compound $Ti\,O_2.Al_2O_3$ is formed, melting at 1,860° C. This compound forms a eutectic with TiO_2 at 15 wt. percent Al_2O_3 and 1,715° C., and a second eutectic with Al_2O_3 at 62 wt. percent Al_2O_3 and 1,850° C. Several low melting fluxes with nonvolatile acid radicals are described.

CONTENTS

I. INTRODUCTION

Titanium dioxide resembles silica in chemical behavior and has found use in the ceramic arts as an opacifying material in enamels and glass. Its high index of refraction might be of value in the preparation of special glasses, if clear titanate glasses can be made. The high melting point of titania makes it useful as a refractory, although it cannot compete at present with the cheaper refractories. However, complete information regarding its value to the ceramic industry can only be gained by a thorough investigation of its reactions with the ceramic materials. The present work deals with the forms of titanium dioxide and its reactions with silica and alumina.

II. THE SYSTEM TiO_2

Titania is found in nature in three crystalline forms, namely, anatase, brookite, and rutile. Anatase is formed whenever titanium hydroxide is dehydrated by heating to a temperature below about 900°.[1] It is reported in the literature [2] [3] that brookite was obtained by laboratory reactions at temperatures between 800° and 1,040°. However, the present work has shown that brookite changes to rutile below this temperature region in the presence of a suitable flux, or mineralizer, and that rutile is formed from anatase above 400°.

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[1] All temperatures are given in degrees centigrade.

[2] P. Hautefeuille, Bull. soc. chim., vol. 5, p. 588, 1863; Compt. rend., vol. 57, p. 148, 1863; vol. 59, p. 188, 1864; vol. 90, p. 868, 1880; Ann. chim. phys. A, vol. 4, p. 131, 1865.

[3] A. Daubree, Ann. mines, vol. 16, p. 129, 1849; Phil. Mag., vol. 9, p. 315, 1855; Edinburgh Phil. Jour., vol. 57, p. 307, 1854; Compt. rend., vol. 29, p. 227, 1849; vol. 30, p. 383, 1850; vol. 39, p. 153, 1853.

Conditions of stability for the natural minerals, without the presence of a mineralizer, have been studied by A. Schröder.[4] He found that anatase can exist in two forms, α and β, which are in equilibrium at 642°, while at 915° ± 15° the α-anatase changes irreversibly to rutile. He also found that brookite changes to rutile with a velocity that is an exponential function of the temperature, the change not being measurable below about 650°. Rutile was not changed to the other forms at any temperature. His results were based on changes in prism angles and densities.

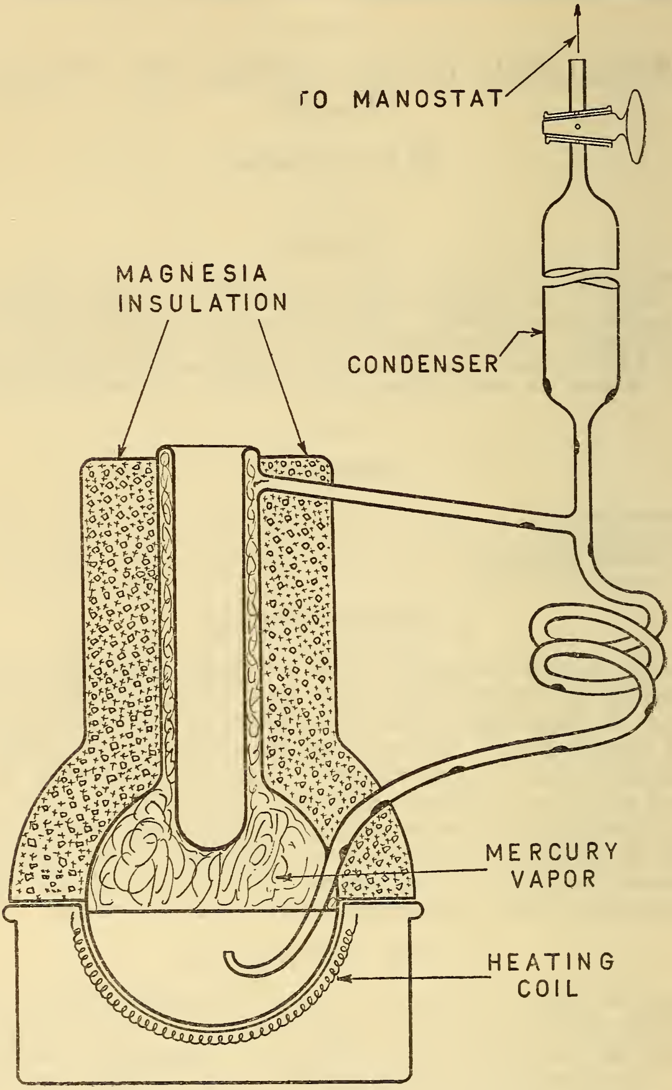

FIGURE 1.—*Mercury vapor thermostat.*

Anatase was prepared from $TiCl_4$[5] by hydrolysis with distilled water, the resulting hydroxide being dried at about 400°. On heating

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[4] A. Schröder, Zeit. Krist., vol 66, p. 493, 1928, and vol. 67, p. 485, 1928.

[5] The $TiCl_4$ was prepared from commercial $TiCl_4$ by S. T. Schicktanz by fractional distillation through a 20-plate still, only the middle fractions being used.

above 1,000°, pure rutile was obtained. Analyses showed these preparations to contain 100.0 percent TiO_2. Brookite was used in the form of finely powdered natural mineral, purified somewhat by repeated extractions with hot hydrochloric acid.

For the experiments described below it was necessary to find suitable low melting fluxes in which TiO_2 would dissolve but with which not all of the sample would react. The vanadates and dichromates were found to be suitable, and the fusion temperatures of some mixtures were determined by the cooling and heating curve method, using about 50 g of stirred material. Melting points of commercial KVO_3, $NaVO_3$, and $LiVO_3$, each containing about 1 percent of carbonate, were found to be 527°, 588°, and 599°, respectively. The minimum melting temperature for KVO_3-$NaVO_3$ mixtures is 480°, at 85 wt. percent KVO_3, and for $NaVO_3$-$LiVO_3$ this temperature is 556°. A minimum melting temperature in KVO_3-$NaVO_3$-$LiVO_3$ is at 461°, with a composition close to 77.6 wt. percent KVO_3-13.4 percent $NaVO_3$-9.0 percent $LiVO_3$. The addition of 10 percent of V_2O_5 to this mixture gives one which is partially molten at 445°. The minimum melting temperature for $K_2Cr_2O_7$-$NaVO_3$ mixtures is 310°, in the neighborhood of 25 wt. percent $NaVO_3$.

A convenient mercury-vapor bath which was used for heating over long periods at temperatures between 300° and 380° is shown in figure 1. It is made of pyrex glass and is filled with nitrogen at a pressure determined by the temperature desired. With changes in room temperature of not more than 3°, the temperature of the bath will remain constant to within about 1°. A 200- to 300-watt heater serves to vaporize the mercury.

Table 1.—*Treatments given anatase seeded with brookite and rutile*

Mineralizer	Temperature	Duration	Result
	°C.	*Hrs.*	
Na_2WO_4	700	24	No change.
Do	725	24	Do.
Do	750	24	Do.
Do	775	24	Do.
Do	790	24	Do.
Do	800	24	All changed to rutile.
Do	840	24	Do.
$NaVO_3$	795	24	Do.
Do	725	24	Do.
$NaVO_3+LiVO_3+K_2Cr_2O_7$	575	24	Do.
$K_2Cr_2O_7$	425	168	No change.
$NaVO_3+KVO_3+LiVO_3$	465	125	Do.
Do	500	48	Do.
Do	515	24	Do.
Do	550	24	Anatase+rutile.
$NaVO_3+K_2Cr_2O_7$	550	24	Do.
Do	525	24	Do.
Do	400	600	Do.[1]
Do	350	700	No change.
$NaVO_3+H_2O$ (in bomb)	350	90	Do.

[1] About 5 to 10 percent rutile. present.

In the presence of mineralizers anatase and brookite will change to rutile at much lower temperatures than those reported by Schröder, as shown in tables 1 and 2. The rate at which anatase is changed to rutile depends upon the flux present as well as upon the temperature. Table 3 shows the treatments given rutile, none of which resulted in changing it.

TABLE 2.—*Treatments given brookite seeded with anatase and rutile*

Mineralizer	Temperature	Duration	Result
	°C.	Hrs.	
$NaVO_3+H_2O$ (in bomb)	350	90	No change.
$K_2Cr_2O_7$	425	24	Do.
$NaVO_3+KVO_3+LiVO_3$	475	24	Do.
Do	525	24	All rutile.
$NaVO_3+K_2Cr_2O_7$	320	1,700	No change.

TABLE 3.—*Treatments given rutile seeded with anatase and brookite*

Mineralizer	Temperature	Duration	Result
	°C.	Hrs.	
Na_2WO_4	725	24	No change.
Do	840	24	Do.
Do	900	24	Do.
Do	950	24	Do.
Do	1,000	24	Do.
Do	1,100	24	Do.
Do	1,200	24	Do.
Do	1,400	24	Do.
$NaVO_3$	600	24	Do.
$NaVO_3+K_2Cr_2O_7$	500	168	Do.
$NaVO_3+KVO_3+LiVO_3$	475	168	Do.
$K_2Cr_2O_7$	425	24	Do.
$NaVO_3+H_2O$ (in bomb)	350	90	Do.
$NaVO_3+K_2Cr_2O_7$	350	700	Do.
Do	325	640	Do.

Identification of the crystal forms of the TiO_2 was made by X-ray spectrograms [6] of the powdered material after all the mineralizer had been thoroughly removed by repeated washings with water, dilute solutions of HCl, and aqueous ammonia. Samples of natural brookite and rutile obtained from the National Museum and anatase prepared artificially were used as identifying standards. All heatings were made in platinum crucibles in an electrically heated tube furnace controlled to ±1°.

The data indicate that if there is a temperature where rutile is in stable equilibrium with anatase or brookite, it must be below 400°.

The melting point of rutile [7] has been reported as 1,560° to 1,980°. Recent determinations by Wartenberg are 1,850° [8] and 1,825°.[9] The melting point, as determined in a hole in an iridium button heated by high-frequency induction [10] was found to be 1,825°. Although this determination can be duplicated within ±5°, a correction of 10° to 20° should be added, as the material would not be visible under exact black body conditions. The white color of anatase changes to a light tan when it changes to rutile, and the color darkens as the rutile is heated to higher temperatures, becoming blue-black on melting.

III. THE SYSTEM TiO_2-SiO_2

The only previous work on this system is that reported by Rieke,[11] who observed the fusion of cones of mixtures heated in a carbon resistance furnace. Considerable reduction of the TiO_2 must have occurred,

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[6] The X-ray spectrograms were made by the metallurgical division of this Bureau.

[7] See J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, vol. 7, Longmans Green, and Co., New York and London. 1927.

[8] Wartenberg and Gurr, Z. anorg. Allgem. Chem., vol. 196, p. 374, 1931.

[9] Wartenberg and Prophet, Z. anorg. allgem. Chem., vol. 208, p. 369, 1932.

[10] See Bunting, B. S. Jour. Research, vol. 4, p. 131, 1930.

[11] R. Rieke, Sprechsaal, vol. 41, p. 405, 1908.

or else he used impure TiO_2, as he found the melting point to be near cone 27, or about 1,600°. Under the reducing conditions in a carbon furnace it is not possible to obtain the correct temperatures for the fusion of binary mixtures containing reducible oxides.

Mixtures of ground quartz crystals (99.7 percent SiO_2) and rutile (100.0 percent TiO_2) were made by wet grinding in an agate mortar. Thorough mixing was further obtained by three fusions, in the oxyhydrogen flame, and intermediate grindings. All mixtures containing not over 20 wt. percent of TiO_2 were heated in a platinum capsule in a rhodium wire resistance furnace for two hours or more before quenching. The phases present in the quenched material were determined with a petrographic microscope. The fusion of mixtures containing over 20 percent TiO_2 was observed in the iridium button.[12] All temperatures were determined on a disappearing filament optical pyrometer [13] and are probably correct to within 10°. The results are shown in table 4 and figure 2. X-ray spectrograms of mixtures containing 40, 50, 57, 65, 70, and 80 wt. percent TiO_2, which were quenched from 1,720°, showed only the presence of rutile crystals. The data show that no compounds are formed and that the eutectic between rutile and cristobalite occurs at 10.5 wt. percent TiO_2 and 1,540° ± 10°.

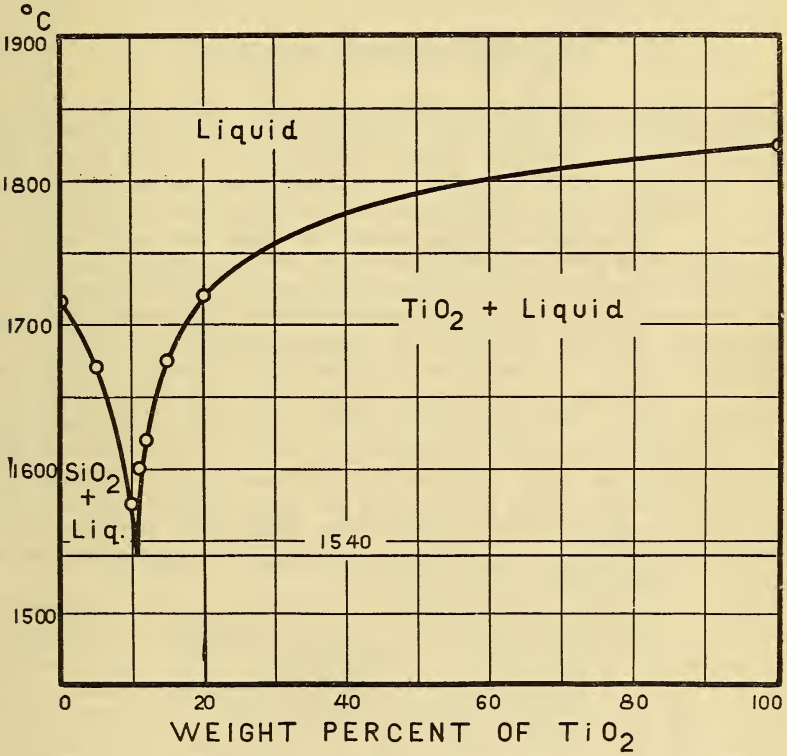

FIGURE 2.—*Phase diagram for the system TiO_2–SiO_2.*

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[12] See footnote 10.

[13] Recently calibrated by the pyrometry section of this Bureau.

Table 4.—*Results with TiO_2–SiO_2 mixtures*

TiO_2 weight	Furnace temperature	Phases present	TiO_2 weight	Furnace temperature	Phases present
Percent			*Percent*		
5	1,670	All glass.	12	1,625	All glass.
	1,665	Glass + cristobalite.		1,620	Glass + rutile.
10	1,580	All glass.	15	1,680	All glass.
	1,575	Glass + cristobalite.		1,675	Glass + rutile.
	1,540	Cristobalite + rutile.	20	1,725	All glass.
11	1,605	All glass.		1,715	Glass + rutile.
	1,600	Glass + rutile.			
	1,540	Cristobalite + rutile.			

IV. THE SYSTEM TiO_2–Al_2O_3

The fusion of mixtures of TiO_2 and Al_2O_3 was observed in the iridium button with the optical pyrometer. The observed fusion temperatures are probably correct to within 25°, since exact black body conditions are not present. Duplicate determinations on small pieces weighing a few milligrams can, however, be checked within about 10°. Determinations on mixtures which are not eutectics or compounds will give temperatures too low, as the mixture will appear to be all melted while some crystals may still be present. Mixtures were prepared from finely ground rutile (100.0 percent TiO_2), and Al_2O_3 (99.95 percent) obtained by igniting aluminum nitrate. The aluminum nitrate was prepared by dissolving aluminum (99.95 percent)[14] in nitric acid of reagent quality and evaporating to dryness in a platinum dish. When ignited to 900°, the Al_2O_3 contained subnitrates equivalent to 0.22 percent N_2O_5, while after ignition at 1,200° only 0.04 percent N_2O_5[15] was found. No determinable quantity of combined nitrogen could be found in the fused Al_2O_3. The mixtures were mixed wet and formed into sticks which were prefused in the oxy-hydrogen flame, using an excess of oxygen to minimize the formation of lower oxides of titanium.

The compositions of the mixtures with their fusion temperatures are given in table 5 and figure 3. The data obtained by Wartenberg and Reusch [16] are also shown. They interpret their data to indicate the formation of the compound $2TiO_2.Al_2O_3$, although they might just as well indicate the compound $TiO_2.Al_2O_3$. The present data indicate the formula $TiO_2.Al_2O_3$ for the compound. As additional evidence, X-ray spectrograms were made of fused mixtures corresponding to these two formulas. The spectrograms showed that the compound is $TiO_2.Al_2O_3$, as no rutile lines were present in the fusion of this composition, while the spectrogram of the $2TiO_2.Al_2O_3$ mixture consisted only of the lines of the TiO_2-Al_2O_3 mixture plus those of rutile.[17] The melting point of $TiO_2.Al_2O_3$ is about 1,860°,

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[14] Analysis by J. A. Scherrer of the Chemistry Division, Bureau of Standards.

[15] Analysis by H. A. Buchheit of the Chemistry Division, Bureau of Standards.

[16] Wartenberg and Reusch, Z. anorg. allgem. Chem., vol. 207, p. 10, 1932.

[17] A microscopic examination by Herbert Insley of the mixture with the composition $TiO_2.Al_2O_3$ which had been fired in the oxy-hydrogen flame showed it to be completely crystalline and to consist wholly of one phase. The crystals had the following optical properties: $\gamma_{Li}=2.015\pm0.01$, $\alpha_{Li}=1.975\pm0.01$, biaxial (−), medium 2V. Extinction parallel with a pronounced prismatic development and good cleavage parallel to α. Pleochroism is strong with α=nearly colorless, γ= deep bluish green. Thick crystals are so deeply colored in the γ direction as to be almost opaque.

and it forms a eutectic with TiO_2 at 15 wt. percent Al_2O_3 and 1,715° and a eutectic with Al_2O_3 at 62 wt. percent Al_2O_3 and 1,850°.

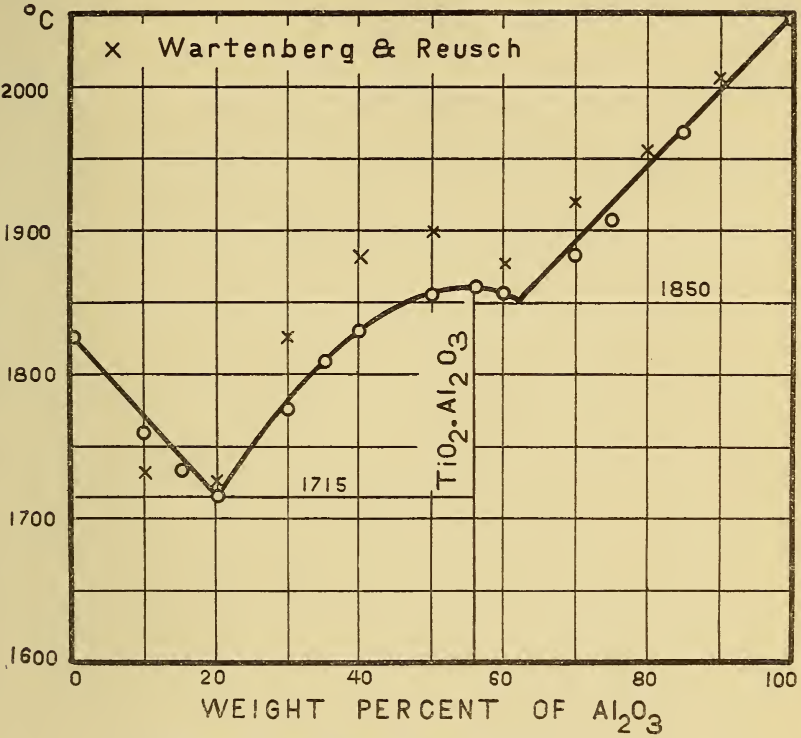

FIGURE 3.—*Phase diagram for the system TiO_2-Al_2O_3.*

TABLE 5.—*Melting points of TiO_2-Al_2O_3 mixtures*

Al_2O_3 weight	Temperature at complete fusion	Al_2O_3 weight	Temperature at complete fusion
Percent	° *C.*	*Percent*	° *C.*
10	1,760	56	1,860
15	1,730	60	1,855
20	1,715	70	1,880
30	1,775	75	1,905
35	1,810	85	1,965
40	1,830	100	2,045
50	1,855		

The writer is indebted to E. W. Washburn, Chief, Chemistry Division, under whose general direction the work was done.

WASHINGTON, August 12, 1933.