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Phase Changes in the ZrO_2-TiO_2 System

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The liquidus curve in the ZrO_2-TiO_2 system previously reported by the present authors was again examined with a heliostat-type solar furnace in order to determine the peritectic point in the ZrO_2-rich side region. Quenched specimens from the melt of the ZrO_2-rich side region were analysed by the X-ray technique. The cooling curves from the melt suggested the existence of a new phase stable at higher temperatures, and a tentative phase diagram at high temperatures is presented.

The phase diagram in the ZrO_2-TiO_2 system has been studied by many investigators. Since the liquidus curve in the system was first published by von Wartenberg[1] in 1931, Sowman and Andrew[2] have demonstrated the results of high-temperature X-ray diffractometry on the ZrO_2-TiO_2 system, while Coughanour *et al.*[3] and later Brown and Duwez[4] proposed the phase diagrams which have been generally accepted up to the present. Recently, however, the subliquidus phase in the diagram was revised by Cocco and Torriano.[5]

Phase changes in the ZrO_2-TiO_2 system were also studied with a heliostat-type solar furnace; the results of the freezing point measurement and of the X-ray analysis of quenched specimens from the melt have been reported by the present authors previously.[6] The subliquidus phase study in the system and the freezing-point data on the specimens between 2.5 and 20 mol% TiO_2 compositions will be supplemented in the present work, and a revised diagram at higher temperatures will be presented.

Apparatus and Materials

In the freezing-point measurements undertaken to obtain additional data, a heliostat-type solar furnace equipped with a brightness pyrometer was used, and the specular reflection method[7,8] reported previously was used. The accuracy of the pyrometer was within $\pm 20°$ at 3000°K and $\pm 15°$ at 2000°K, including the reading error for oscillograms.

ZrO_2 99.8% pure (including about 1.8% HfO_2) from the Yokozawa Chemicals Co., Tokyo, and TiO_2 99.7% pure from the Kanto Chemicals Co., Tokyo, both used in the previous work, were carefully mixed in an agate mortar and then heated in an electric resistance furnace at 1500°C for 3 hr. After two grinding and heating cycles, the specimen was pressed into a $6 \times 6 \times 30$ mm bar under 4000 kg/cm^2 pressure without any lubricant or binder for the freezing-point measurements. No repeated fusion was made for the sample preparation in order to avoid any deviation from the stoichiometry of the composition at higher temperatures and also any contamination by impurities resulting from the grinding process and pressing.

X-Ray diffraction measurements of the quenched specimen were made using a diffractometer on a Shimadzu diffraction unit GX-3 and by nickel-filtered CuKα radiation. High-temperature X-ray diffraction data were obtained with a Shimadzu HX-II model, the hot stage of which consists of a platinum-rhodium-wound heating element encased in an alumina refractory sleeve. Temperature measurements were made with platinum *versus* platinum-10% rhodium thermocouple.

Results and Discussions

Freezing-point Measurements. On the basis of the results of Cocco and Torriano, who claimed to have found a solid solution boundary between tetragonal zirconia and the two phase region (tetragonal zirconia plus $ZrTiO_4$) of 15mol% TiO_2 at elevated temperatures, the former anomaly in the liquidus curve reported by the authors was again examined in the compositions containing between 2.5 and 17.5 mol% TiO_2.

1) H. von Wartenberg and W. Gurr, *Z. anorg. Chem.*, **196**, 374 (1931).
2) H. G. Sowman and A. I. Andrew, *J. Am. Ceram. Soc.*, **34**, 298 (1951).
3) L. W. Coughanour *et al.*, *J. Res. Natl. Bur. Standards.*, **52**, 37 (1954).
4) F. H. Brown and P. Duwez, *J. Am. Ceram. Soc.*, **37**, 129 (1954).
5) A. Cocco and G. Torriano, *Annali di Chimica.*, **55**, 153 (1965).
6) T. Noguchi and M. Mizuno, *Solar Energy.*, **11**, 7 (1967).
7) T. Noguchi and T. Kozuka, *ibid.*, **10**, 125 (1966).
8) T. Noguchi and M. Mizuno, This Bulletin, **41**, 1583 (1968).

The seven specimens, in 2.5 mol% TiO_2 increments, were fused by means of the solar furnace, and their freezing temperatures were obtained from the cooling curves and spectral emissivity measurements. The cooling curves for each specimen were measured, using a dual-beam cathode ray oscilloscope, at several points across the sun's image under various heating temperatures after the thermal equilibrium had been attained. The thermal equilibrium was attained wihtin several seconds[9] from the attenuater opening. The measurements were repeated on different parts of the specimen surface more than thirty times in order to confirm the homogeneity of the composition in the specimen; the data agreed within the limits of error of the pyrometer reading. The cooling curves for each composition are shown schematically in Fig 1. The spectral reflectivity was also measured in order to obtain the spectral emissivity at 0.65μ near and at the respective freezing-point.

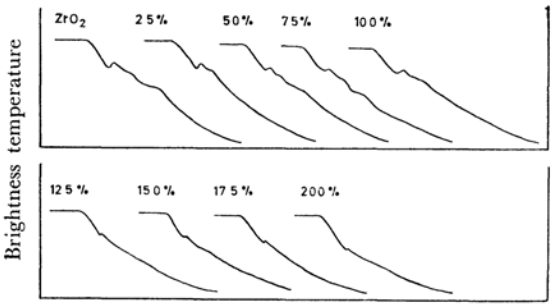

Fig. 1. Schematic cooling curves of the compositions containing TiO_2 up to 20 mol percent.

Table 1. Freezing point data of the compositions containing TiO_2 up to 20 mol percent

TiO_2 content (mol%)	Freezing point (±20°C)	Spectral emissivity at 0.65 μ	Temperature of* exothermic peaks in solid state (°C)	
0**	2706	0.81	—	—
2.5	2701	0.83	2487	—
5.0	2655	0.87	2498	2338
7.5	2618	0.84	2484	2332
10.0**	2580	0.95	2468	—
12.5	2495	0.94	—	—
15.0	2395	0.92	—	—
17.5	2343	0.96	—	—
20.0**	2316	0.92	—	—

* These values were calculated from their brightness temperatures and the emissivity data at the respective freezing point.
** Quoted from the previous work by the authors.

The average values of the freezing temperature for each composition are listed in Table 1, along with the spectral emissivity data. The results show that the anomaly in the liquidus curve is shifted from 20 mol% to 17.5 mol% TiO_2.

Chemical Analysis of Quenched Specimens. In order to examine the stoichiometry of the composition in specimens fused with the solar furnace in air, chemical analysis was made on specimens containing 10, 20, 30, 50 and 70 mol% TiO_2. The specimens were kept about 100°C higher than the respective melting temperatures for 3 min.*1 Because of the difficulty in separating TiO_2 from ZrO_2, the ZrO_2 content in the specimen was determined by the following method.

A weighed specimen of about 50 mg in a platinum crucible was fused with the addition of ten times as much sodium pyrosulfate and then dissolved with nitric acid into a sample solution. After the addition of an excess amount of an EDTA standard solution (0.009594 M), a 10% solution of ammonium tartarate was added; the pH of the sample solution was then adjusted to between 1—2 with nitric acid or ammonia water. The sample solution was heated for five minutes and then back-titrated with a bismuth nitrate standard solution (0.017669M) using the XO indicator. The end point was shown by the color change from yellow to red purple; the results are shown in Table 2.

The ZrO_2 content was determined by the spectrochemical analysis to contain about 1.8% HfO_2, which was calculated as ZrO_2. Therefore, a correction was made in examining the stoichiometry,

Table 2. Results of chemical analysis on quenched specimens from the melt

Sample	ZrO_2 content % (theoretical)	ZrO_2 content % (determined)	Corrected values		Deviation from theoretical value mol%
			wt%	mol%	
ZT-2	93.28	92.01	93.2	89.9	−0.1
ZT-3	86.05	85.00	86.1	80.1	+0.1
ZT-4	78.25	77.31	78.3	70.1	+0.1
ZT-6	60.66	59.52	60.3	49.6	−0.4
ZT-8	39.79	39.53	40.0	30.2	+0.2

9) T. Noguchi and T. Kozuka, *Solar Energy.*, **10**, 203 (1966).
*1 Several seconds were necessary for the fusion of a specimen with the solar furnace, and several additional seconds were required to attain the thermal equilibrium. Therefore, the time for the cooling curve measurements was about 10 sec.

and the deviation from the theoretical values was found to be less than 0.4 mol%. The titanium content in the fused TiO_2 specimen was determined by the gravimetric method. The composition was found to be $TiO_{1,997}$ and to agree with the results of Bauer and Littke.[10]

X-Ray Diffraction Data

X-Ray diffraction measurements were made on quenched specimens from the melt and on those heated at 1700°C for 6 hr in an electric-resistance furnace. The molten specimens were prepared with the solar furnace by heating them to about 100°C higher than the respective melting points for 20 sec before quenching. The diffraction data are listed in Table 3, along with the data on the ZrO_2-TiO_2 system obtained in a previous paper.

The single phase of the $ZrTiO_4$ compound was observed on the specimen (1:1) heated at 1700°C, while the quenched specimen from the melt showed

Table 3. X-ray diffraction data on the quenched specimens in ZrO_2-TiO_2 system

Compositions (mol%)		Results of X-ray diffraction					
		1700°C			Solar furnace melt		
ZrO_2	TiO_2						
97.5	2.5	M			M		
95.0	5.0	M			M		
92.5	7.5	M			M		
90.0	10.0	M			M		
87.5	12.5	M			M		
85.0	15.0	M			M	ZT	
82.5	17.5	M	ZT		M	ZT	
80.0	20.0	M	ZT		M	ZT	
75.0	25.0	M	ZT				
70.0	30.0	M	ZT		M	ZT	*
65.0	35.0	M	ZT				
62.0	38.0	M	ZT				
60.0	40.0	M	ZT		M	ZT	R*
59.0	41.0	M	ZT				
56.0	44.0		ZT				
55.0	45.0		ZT		M	ZT	R*
53.0	47.0		ZT				
50.0	50.0		ZT		M	ZT	R*
49.0	51.0		ZT				
47.0	53.0		ZT				
45.0	55.0		ZT		M	ZT	R*
40.0	60.0		ZT	R		ZT	R*
30.0	70.0		ZT	R		ZT	R*
20.0	80.0		ZT	R		ZT	R*
10.0	90.0			R			R*

* Quoted from the previous work by the authors.
Note: M: monoclinic ZrO_2 solid solution,
ZT: $ZrTiO_4$ s. s. R: TiO_2 s. s.

10) G. Bauer and W. Littke, *J. Inorg. Nucl. Chem.*, **16**, 67 (1960).

three components, $ZrTiO_4$, monoclinic ZrO_2, and tetragonal TiO_2 as an incongruently melting material. The lattice parameters of the $ZrTiO_4$ solid solution with compositions containing 35 to 60 mol% TiO_2 were obtained using the diffraction lines from (032), (014) and (400) with the scanning speed of 2θ 1/8° min for the specimens fired at 1700 °C. Both a and c axes contracted from 41 mol% composition, and the unit cell volume increased from a 50 mol to a 53 mol% composition. Moreover, the boundaries of the $ZrTiO_4$ solid solution for ZrO_2 and TiO_2 sides at 1700°C were located at 41 mol% and 53 mol% TiO_2 respectively, as is shown in Fig. 2.

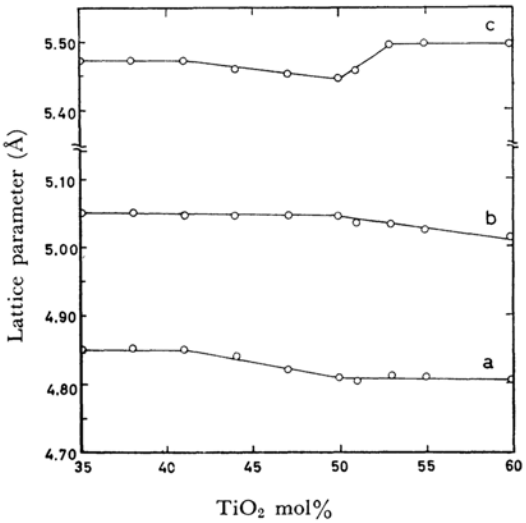

Fig. 2. Lattice parameters of $ZrTiO_4$ solid solutions.

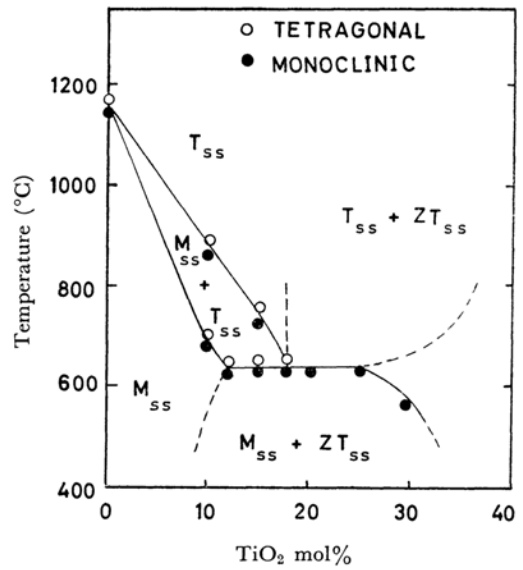

Fig. 3. High temperature X-ray diffraction data in ZrO_2 rich side region.

The specimens containing up to 30 mol% of TiO_2 were fired at 1700°C for 3 hr and then examined by high-temperature X-ray diffractometry in order to determine the solid solution boundaries at lower temperatures. The diffraction data were obtained from 2θ 27° through 33° and by the heating and cooling rates of 2°C/min. The average values obtained by five heating and cooling cycles are shown in Fig. 3; the data agreed with Cocco's results, which differ from those of Duwez, who estimated the solid solution boundary on the basis of the thermal expansion measurement. However, the boundary between tetragonal and monoclinic ZrO_2 solid solutions in the present work seems to be about 140°C higher than that obtained by Cocco. Moreover, this boundary was not straight with the increase in the TiO_2 content, the transformation temperature decreasing, as was claimed by Duwez.

The lattice parameters of the monoclinic solid solution in the specimens quenched from the melt and at 1700°C are shown in Fig. 4. The quenching rate from the melt was about 2300°C/sec. The data were obtained with the diffraction lines from (111), (11$\bar{1}$), (011), and (00$\bar{2}$).

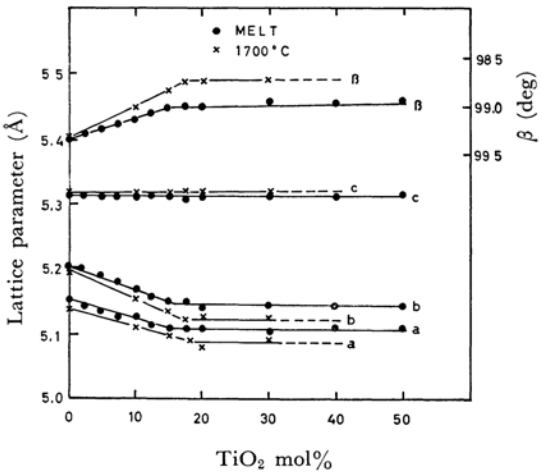

Fig. 4. Lattice parameters of monoclinic ZrO_2 solid solution.

While the solubility limit of TiO_2 in a $ZrTiO_4$ solid solution in the specimens quenched from the melt was previously found at 80 mol% TiO_2, the quenched specimen from 1700°C showed a solid solution boundary at 83.5 mol% TiO_2.

Phase Diagram

Tentative additions to the phase diagram in the ZrO_2-TiO_2 system were made to the revised diagram by Cocco and Torriano, using the liquidus curve in the system shown in Fig. 5.

Pure zirconia has shown the exothermic peaks[7] at 2494° and 2325°C respectively, while the latter

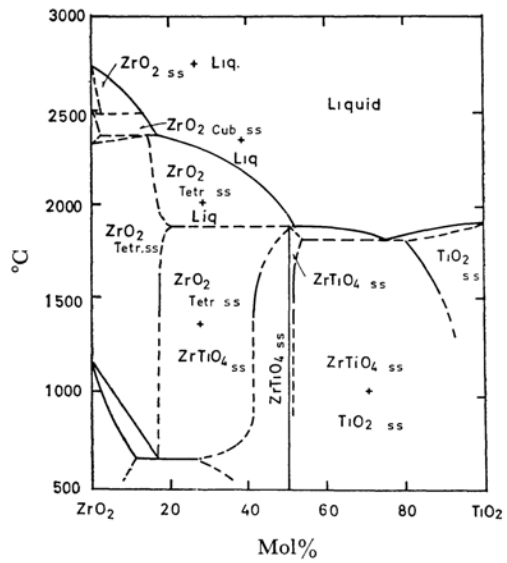

Fig. 5. Tentative phase diagram of ZrO_2-TiO_2 system at high temperature.

was estimated to be the transformation from a cubic to a tetragonal modification of ZrO_2. The very weak exothermic peaks which appeared in the cooling curves of the compositions containing 2.5, 5, 7.5 and 10 mol% TiO_2 in the solid state*2 were observed at temperatures slightly lower than 2500 °C. Although the high accuracy in the temperature measurement upon a transformation in the solid state can not usually be expected by such a dynamic method, the ZrO_2 modification in this region was not frozen by the quenching rate in the present work and was considered to show a diffusionless phase change.[11] Therefore, the accuracy of these values were estimated to be close to that obtained in the freezing-point measurements. A complete interpretation of these phenomena was not possible in the present work; however, a transformation from a stable form at above 2500°C to a cubic form might be suggested on the basis of the experimental evidence in establishing the phase relation on the ZrO_2-rich side region at very high temperatures. The existence of a very narrow two-phase region was assumed without actual experimental proof below 2500°C in order to satisfy the phase rule. The highly speculative hypothesis developed by Sense[12] that ZrO_2 may have the monoclinic crystal structure and be quenchable might not be acceptable in the present work, though the crystal structure of zirconia above 2500°C is not yet known. The lattice parameters of zirconia specimens of both the green and those quenched

*2 The freezing point was confirmed by visual observation through the ocular lens of the brightness pyrometer and with both oscillograms and data from the automatic voltage-recording meter.

11) G. M. Wolten, *J. Am. Ceram. Soc.*, **46**, 418 (1963).
12) K. A. Sense, *ibid.*, **44**, 465 (1961).

from the melt showed no remarkable difference within the limits of accuracy of the measurements. An electron micrograph of the quenched zirconia from the melt showed a crack on the thermally-etched surface as in the previous paper.

The second exothermic peaks appearing in the solid state were slightly higher than the transition point from the cubic to the tetragonal form of ZrO_2; the temperatures of these points, almost identical to the freezing temperature of the 17.5 mol% TiO_2 composition, accounted for the solidus line.

The solid solution boundary between tetragonal ZrO_2 and the two-phase region of tetragonal ZrO_2 plus $ZrTiO_4$ under the solidus line was located at 15 mol% TiO_2, while that at 1700°C was located at 17.5 mol% TiO_2 (*cf.* Fig. 4).

The other parts of the diagram were based on the following experimental results:

1) The solid solution boundaries between tetragonal and monoclinic forms of zirconia, and other two-phase regions at lower temperatures, as is shown in Fig. 3.

2) The solid solution boundaries of $ZrTiO_4$ for both ZrO_2 and TiO_2 sides.

3) The solid solution field of TiO_2.

Conclusions

The anomaly in the liquidus curve in the ZrO_2-TiO_2 system has been found at 17.5 mol% TiO_2. A tentative phase diagram for the ZrO_2-TiO_2 system at higher temperatures has been presented, and the existence of a new high-temperature modification of ZrO_2 above 2500°C has been suggested. Further, the phases of ZrO_2 at very high temperatures should be examined by a dynamic method such as high temperature X-ray diffractometry with imaging furnaces.

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