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Liquidus Curve Measurements in the ZrO_2-MgO System with the Solar Furnace

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A liquidus curve in the system ZrO_2-MgO was investigated by the use of a heliostat type solar furnace. The cooling curves of a composition were obtained by the specular reflection method with a brightness pyrometer. Quenched specimens from the melt were examined with an X-ray technique and a petrographic microscope. Newly found anomalies on the liquidus curve were 7.5, 12.5 and 17.5 mol% MgO compositions. The composition of 12.5 mol% MgO quenched from the melt showed the new cubic-like phase of which optic angle of $2V$ equals to $-74°$ and decomposed easily into monoclinic and tetragonal forms by reheating at 1300°C.

Many papers have been published on the phase study of the ZrO_2-MgO system up to present, and the earlier works on the system were surveyed by Dietzel and Tober[1] in 1953. The melting diagram was first studied by von Wartenberg and Werth[2] in 1928 who proposed two eutectic points with 10 and 48 wt% MgO at about 1630 and 1600°C respectively, and with a maximum point with the composition of ZrO_2·MgO at about 2120°C. Ebert and Cohn[3] claimed that an eutectic point with 50 mol% MgO at 2100°C in 1933, and the same result was also estimated by Zirnowa[4] at 2070°C in 1939. Later the subliquidus phase of the system in ZrO_2 side below 2000°C was investigated by Dietzel and Tober, and also Duwez *et al.*[5] in 1952. Recently the phase boundary of the cubic ZrO_2 solid solution above 2000°C was reported by Hinz and Dietzel[6] in 1962, and by Viechnicki and Stubican[7] in 1965 respectively.

However, the data on the liquidus curve on the system with sufficient accuracy have not been published yet. The authors reported on the high temperature phase in ZrO_2-CaO system using a heliostat type solar furnace previously[8] and anomalies on the liquidus curve were found in ZrO_2 rich side region. This paper relates to the liquidus curve measurement on the ZrO_2-MgO system, in which the behaviors of magnesia are similar to those of calcia in the stabilization of zirconia refractory.

Equipment and Materials

The temperature and emissivity measurements were performed with the brightness pyrometer at 0.65 μ by the specular reflection method as reported by the author previously.[9] The standard deviation derived in the transmission measurement of the grey filter in the pyrometer was 1.7% and therefore the recorded value was estimated to be reliable within the error of about 2% as an amount of radiant energy. This corresponds to 10° at 3000°K and 15° at 4000°K calculating from Planck's equation respectively. These values were verified by the calibration with the tungsten filament standard lamp at the focal plane of the solar furnace, and the accuracy of the brightness pyrometer at 3237°K was within $\pm 7°$.[10] The accuracy of derived temperatures in this experiment was thus estimated to be within $\pm 20°$ at 3000°K and $\pm 15°$ at 2000°K including the reading errors of oscillograms. The heliostat type solar furnace used was the combination of the paraboloid of 1.5 m in diameter and 64 cm of focal length, and the heliostat plane mirror of 2.4×2.4 m with sixteen segments of front coated glass. The optical axis of the paraboloidal mirror was fixed horizontally.

Materials used were ZrO_2 of 99.8% purity from the Yokozawa Chemicals Co., Tokyo (including about 1.8% of HfO_2, and ignition loss, 0.05; Cl, 0.04; SO_4, 0.008; Fe, 0.001%) and MgO of 99.7% from the Kanto Chemicals Co., Ltd., Tokyo (ignition loss, 0.11; Cl, 0.002; heavy metal, 0.002; Fe, 0.0004; Zn, 0.002; Ba, 0.0025; Ca, 0.102%). The starting materials were carefully mixed in an agate mortar, calcined in an electric resistance furnace at 1700°C for 6 hr by two heating and grinding cycles, and pressed into $6 \times 6 \times 35$ mm bar under 4000 kg/cm^2 without any lubricant or binder.

1) A. von Dietzel and H. Tober, *Ber. Dtsch. Keram. Ges.*, **30**, 47 (1953).
2) H. von Wartenberg and H. Werth, *Z. anorg. u. allgem. Chem.*, **190**, 178 (1930).
3) F. Ebert and E. Cohn, *ibid.*, **213**, 321 (1933).
4) N. Zirnowa, *Zhur. Priklad. Khim.*, **12**, 1278 (1939).
5) P. Duwez, F. Odell and F. H. Brown, Jr., *J. Am. Ceram. Soc.*, **35**, 107 (1952).
6) I. Hinz and A. Dietzel, *Ber. Dtsch. Keram. Ges.*, **39**, 530 (1962).
7) D. Viechnicki and V. S. Stubican, *J. Am. Ceram. Soc.*, **48**, 292 (1965).
8) T. Noguchi, M. Mizuno and W. M. Conn, *J. Solar Energy*, **11**, 136 (1967).
9) T. Noguchi and T. Kozuka, *ibid.*, **10**, 125 (1966).
10) S. Takada, H. Ito, T. Noguchi and T. Kozuka, *Report Nat. Res. Lab. Metrology*, **16**, 206 (1967).

Eleven specimens in 10 mol% MgO increments and nine specimens in 2.5 mol% increments from 2.5 to 30 mol% were prepared by the heat treatment as referred to the previous study on ZrO_2-CaO system. Four specimens in 5 mol% MgO increments from 30 to 70 mol% were also added to confirm the eutectic points.

Results and Discussion

Freezing Point Measurement. On the sun's image of 6 mm in diameter on the specimen surface, the variation of the brightness temperature in the area of 0.25 mm ϕ was measured with the brightness pyrometer. The cooling curves of the specimen were obtained with the dual-beam cathode-ray oscilloscope (Multiscope VP 541 A) attached with the Polaroid camera and were shown schematically in Fig. 1. The freezing and melting temperatures of the specimen were also confirmed by the visual observation through the ocular lens of the pyrometer and by the data from the automatic voltage recorder. The cooling rate of the specimens was estimated from 1800 to 2300 deg/sec. The exothermic peak observed after the freezing point might be ascribed to the phase transformation in solid state.

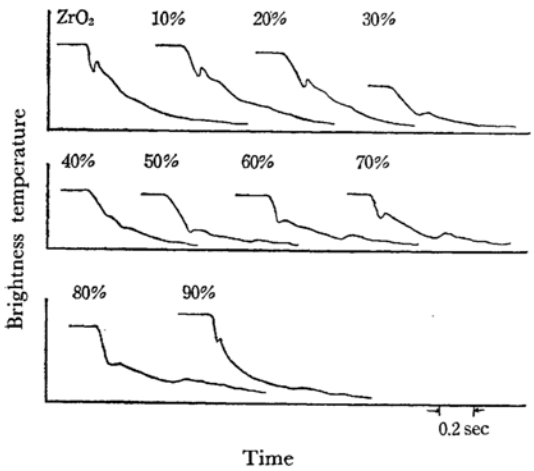


Fig. 1. Cooling curves of the composition in ZrO_2-MgO system.

ZrO_2 showed two weak exothermic peaks accompanied with the crystallization and the similar phenomenon was observed up to 25 mol% MgO composition. In the fusion of MgO specimen vigorous vaporization was observed and failed to give the emissivity data. Only the brightness temperature of the freezing point was hardly obtained and it was difficult to hold the specular reflection surface because of the deposition of vaporized magnesia on the specimen surface. No correction for transmission of magnesia vapor was also possible.

Figure 2 represents the freezing point data obtained in the ZrO_2-MgO system. The freezing point is indicated as the true temperature and both of the 2nd and the 3rd exothermic peaks observed in solid state are indicated by the brightness temperature. The mean value of forty to fifty individual readings on the freezing point is listed in Table 1 with the spectral emissivity data at 0.65 μ. Only the freezing point of MgO was cited from the

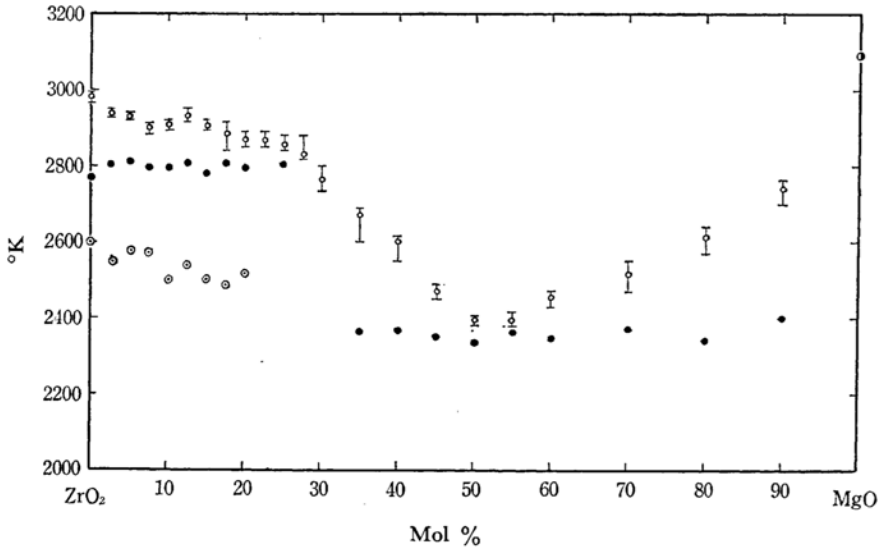


Fig. 2. Freezing point data in the ZrO_2-MgO system.

- ● The 2nd exothermic peak in solid state
- ○ Freezing point
- ⊙ The 3rd exothermic peak in solid state
- ◑ Cited from McNally *et al.*

TABLE 1. FREEZING POINT DATA OF ZrO_2-MgO SYSTEM

Composition ZrO_2 (mol%)	MgO (mol%)	Freezing point (±20°C)	Spectral emissivity at 0.65 μ	Temperature* of exothermic peaks in solid state (°C)	
97.5	2.5	2660	0.89	2528	2270
95	5	2647	0.90	2525	2295
92.5	7.5	2622	0.92	2512	2296
90	10	2632	0.95	2513	2224
87.5	12.5	2650	0.86	2531	2259
85	15	2633	0.94	2501	2217
82.5	17.5	2598	0.88	2518	2212
80	20	2594	0.90	2517	2235
77.5	22.5	2589	0.94	2532	
75	25	2576	0.91	2530	
72.5	27.5	2547	0.90		
70	30	2486	0.93		
65	35	2403	0.87	2078	
60	40	2329	0.90	2090	
55	45	2196	0.93	2073	
50	50	2121	0.90	2080	
45	55	2113	0.93	2054	
40	60	2171	0.96	2064	
30	70	2230	0.95	2087	
20	80	2332	0.96	2054	
10	90	2458	0.93	2116	

* These values were calculated as brightness temperature.

literature[11] because of the difficulty in obtaining the emissivity data and accordingly the true temperature. Anomalies not reported in the liquidus curve previously were found to be at 7.5, 12.5 and 17.5 mol% MgO compositions, showing the maximum point at 12.5 mol%. The tendency of this type was similar to those in ZrO_2-CaO system in ZrO_2 side region, though the maximum point shifted to 7 mol% CaO composition.

It should be noted that the solid state reaction observed in some of these cooling curves in the ZrO_2 rich side region could not be suppressed by the quenching rate as in this study. Since the specimen is heated from its surface at the focus of the solar furnace, the liquid phase formed at the solar image is surrounded by the solid even if the thermal equilibrium is obtained. Therefore, the solid crystal under the liquid layer might become the nuclei on crystallization and accelerate the growth of crystals in the cooling process.

Stoichiometry. The specimen for chemical analysis was prepared with the solar furnace in such a way that a test bar was fused at about 100°C higher than the respective melting temperature for 3 min before quenching. Since the necessary time for each measurement of cooling curve was within 10 sec and repeated measurements across the sun's image were made on five different points in three times, simulation for the heat treatment of a specimen might be considered satisfactory.

The weighed sample of about 50 mg in a platinum crucible was fused with the addition of tenfold sodium pyrosulfate. The extraction with dil. H_2SO_4 (5%) was neutralized with NH_4OH by the addition of NH_4Cl. The pH of the filtrate was then adjusted to 10 and the sample solution was titrated with EDTA solution by the aid of KCN and BT indicator. The results obtained are shown in Table 2 and the deviation of MgO component is clearly observed. These data differ from those claimed by Hinz and Dietzel who applied the argon plasma torch because of the estimated heating temperature of more than 5000°K.

TABLE 2. CHEMICAL ANALYSIS OF QUENCHED SPECIMENS FROM THE MELT BY CHELATE TITRATION IN THE ZrO_2-MgO SYSTEM

Sample	MgO content (Theoretical) wt%	MgO content (Determined) wt%	MgO content (Determined) mol%	Difference mol%
M 10	3.51	3.00	8.64	−1.36
M 30	12.29	9.65	24.61	−5.39
M 40	17.91	14.57	34.26	−5.74
M 50	24.66	21.27	45.22	−4.78
M 60	32.92	29.58	56.21	−3.79
M 70	43.29	36.56	63.78	−6.22
M 90	74.65	62.79	83.76	−6.24

The vaporization rates at melting temperatures for ZrO_2, 50 mol% MgO composition and MgO specimens which were prepared by sintering at 1700°C for 3 hr are 5.3×10^{-4}, 2.3×10^{-3}, and 9.0×10^{-3} g/cm^2 min respectively. These values were obtained by heating the specimen of about 1.5 g and were estimated from the weight decrease in 10 min. Even for the short heating duration as in the experiment, the vaporization of MgO can not be suppressed in air because of the high vapor pressure near the melting point.

X-Ray Analysis of Quenched Specimens from the Melt. The quenched specimens were examined by X-ray technique using a diffractometer of the Shimadzu Diffraction Unit GX-3 and nickel filtered Cu$K\alpha$ radiation. High temperature diffraction patterns were obtained using the Shimadzu HX-II model whose hot stage consists of a platinum-rhodium wound heating element encased in an alumina refractory sleeve. The temperature measurement was made with a platinum *versus* platinum-10% rhodium thermocouple. The results of the powder diffraction patterns of the quenched specimens are shown in Table 3, and sufficient explanation on the anomalies in the liquidus curve was not obtained.

In ZrO_2 rich side region up to 15 mol% MgO composition, the diffraction patterns showed broadening and were not identified as cubic form.

11) R. N. McNally, F. I. Peters and P. H. Ribbe, *J. Am. Ceram. Soc.*, **44**, 491 (1961).

TABLE 3. X-RAY DIFFRACTION DATA OF QUENCHED SPECIMENS IN ZrO_2-MgO SYSTEM

Composition MgO mol%	Phase present after quenching		
2.5	M(s)		
5.0	M(m)	C*(m)	
7.5	M(vw)	C*(s)	
10.0	M(vvw)	C*(s)	
12.5		C*(s)	
15.0		C (s)	
17.5		C (s)	
20.0		C (s)	
25.0		C (s)	
30		C (s)	MgO(vw)
35		C (s)	MgO(vw)
40		C (s)	MgO(m)
50		C (s)	MgO(m)
60		C (s)	MgO(m)
70		C (s)	MgO(s)
80		C (s)	MgO(s)
90		C (m)	MgO(s)

M: Monoclinic ZrO_2 solid solution,
C: Cubic ZrO_2 solid solution,
C*: Cubic not resolved.

The slow scan pattern of 12.5 mol% MgO composition at 2θ 1/8° min gave no extra reflection up to 2θ 160°, as compared with that of 7 mol% CaO composition. Cubic zirconia was widely observed in the system except the ZrO_2 rich side region. Periclase coexisted from 30 mol% MgO composition through MgO side.

The lattice parameters of cubic zirconia solid solution were obtained from diffraction lines with $2\theta > 85°$ on 12.5 to 70 mol% MgO compositions and the boundary for the cubic zirconia solid solution in the quenched specimen from the melt was located at about 25.5 mol% MgO as shown in Fig. 3, almost identical to the results claimed by Duwez *et al.* at 2000°C. It might be assumed that the solid solution boundary for cubic zirconia above 2000°C up to melting temperature was vertical.

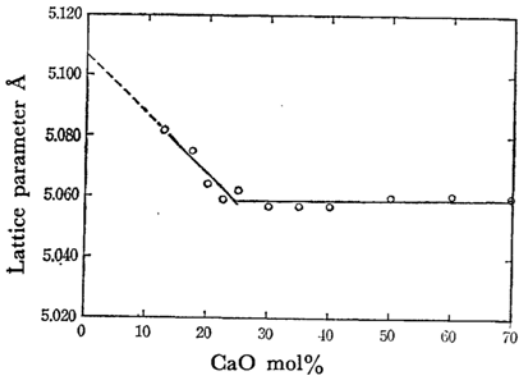


Fig. 3. Lattice parameters of cubic ZrO_2 solid solution.

The lattice parameters of magnesia from 40 to 100 mol% MgO were measured with diffraction lines with $2\theta > 95°$ and were constant at 4.211 Å. Very narrow region for the tetragonal zirconia solid solution *i. e.* the solid solution boundary between tetragonal zirconia and tetragonal zirconia plus magnesia might be assumed at less than 5% of MgO from the results in Table 3.

High temperature X-ray diffraction patterns on the quenched specimens of 5, 10, 12.5, 17.5 and 30 mol% MgO compositions were obtained on 2θ 20—45° and with heating and cooling rates of 20°C/min from 500 to 1300°C. No remarkable change was observed at the heating process and the tetragonal form was not found even at 1250°C except 5 mol% composition. However, in the specimens of 5, 10, 12.5 and 17.5 mol% MgO compositions the monoclinic form appeared at 900—850°C on cooling, and a decomposition of the 12.5 mol% MgO composition into tetragonal and monoclinic forms was observed as in the case of 7 mol% CaO composition.

Microscopic Observation on the Quenched Specimens. The thin section of the quenched specimens in ZrO_2 rich side region from the melt was examined by the petrographic microscope. The analytical data are shown in Table 4.

TABLE 4. MICROSCOPIC DATA ON ZIRCONIA MODIFICATIONS IN THE QUENCHED SPECIMENS IN ZrO_2-MgO SYSTEM

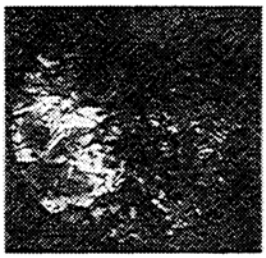
Composition MgO mol%	Monoclinic	Tetragonal	Biaxial negative $2V=-74°$	Isotropic cubic
2.5	+++++			
3	+++	++		
4	++	+++		
6		+++	+++	±
8		+	++++	±
10			+++++	
12.5			+++++	
15			++	++−

The biaxial negative crystals were found besides the monoclinic, tetragonal and cubic forms. The optic angle of the crystals was $2V=-74°$ and different to that of the monoclinic form of −30°. The single phase of this modification is limited at about 12.5 mol% MgO composition and Fig. 4 shows the photomicrographs of 3, 12.5 and 15 mol% MgO compositions quenched from the melt. Thus the new cubic like phase might be assumed to be rhombic modification rather than the distorted cubic lattice, though the verification of the presence of this form was not possible by the X-ray diffraction data.

Liquidus Curve in the ZrO_2-MgO System. The liquidus curve obtained by the freezing point measurements was corrected in relation to the

a) 3 mol% MgO composition

b) 12.5 mol% MgO composition



c) 15 mol% MgO composition ×180 Crossed nicols.

Fig. 4. Photomicrographs of the thin section of zirconia modifications in the specimens quenched from the melt.

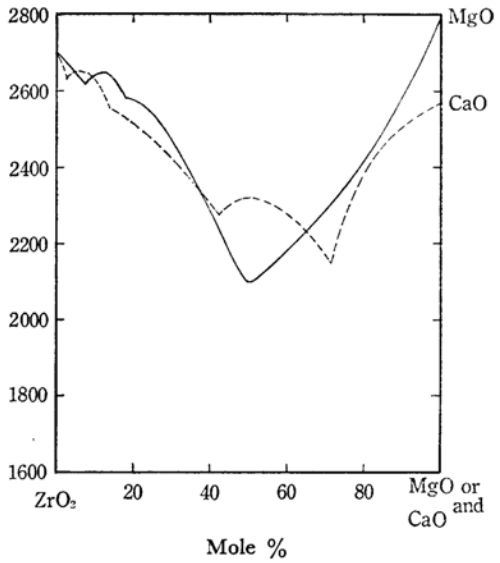


Fig. 5. Liquidus curve in the system ZrO_2-MgO.

chemical analysis of the quenched specimens from the melt and is shown in Fig. 5 with that of the ZrO_2-CaO system. The characteristic anomaly in ZrO_2 rich side region shifts to about 10 mol% MgO. The behaviors of MgO in this region at higher temperatures were not understood sufficiently because of the lack of knowledge on the crystal modification above 2300°C to present the complete phase diagram on the system. However, the maximum point observed in ZrO_2 rich side region might indicate the existence of a new cubic like phase, which decomposed easily after reheating into monoclinic and tetragonal forms. The anomalies in this experiment were not reported by the previous investigators. Ebert and Cohn[3] have assumed an peritectic point in this region without experimental evidences, however, the accuracy of temperature measurement by them was not described clearly, and it might be estimated within ±50°C at more than about 2500°C by a visual observation method. The eutectic point was found at 50 mol% MgO at 2113 ±15°C. And the other compound such as $Mg_2Zr_3O_8$ or $MgZr_3O_7$ reported in the earlier literatures[1] were not confirmed from this experiment. It is noted that the phase study in ZrO_2 rich side region above 2300°C should be further developed.

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