BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2614—2616 (1970)

The Liquidus Curve of the ZrO_2-Y_2O_3 System as Measured by a Solar Furnace

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(Received November 19, 1969)

A subliquidus phase in the ZrO_2-Y_2O_3 system was studied by Duwez *et al.*,[1] who claimed an eutectic with 70 mol% Y_2O_3 at 2100°C and a peritectic at 2500°C, and by Otto[2] who claimed them at 2260°C and 2580°C respectively. More recently (1962) Fu-Kan *et al.*[3] have reported on a subliquidus-phase study of the system and demonstrated $Y_2Zr_2O_7$ compound at 2530±30° C. Liquidus curves in the ZrO_2-Ln_2O_3 systems[4] and the phase diagram of the ZrO_2-Y_2O_3 system[5] were also studied at the Ultra-Refractory Laboratory of Mont-Louis, France, using a heliostat-type solar furnace. The present authors have previously studied the high-temperature phases in ZrO_2–CaO[6] and ZrO_2–MgO[7] systems with a heliostat-type solar furnace; we found anomalies in the liquidus curves in the ZrO_2-rich side region. This note will be concerned with the liquidus curve measurement in the ZrO_2-Y_2O_3 system and with anomalies in the curve of the system.

Experimental

By the use of a brightness pyrometer the freezing points of a composition in the ZrO_2-Y_2O_3 system were measured by means of the specular reflection method.[8] The brightness temperature of the freezing point of the respective composition was obtained from the cooling curve. The spectral reflectivity of the specimen was also measured at 0.65 μm by the use of a shadowing plate, and the spectral emissivity was estimated from the reflectivity data. Thus, the true temperature of the freezing point was calculated. The materials used were ZrO_2 (99.8% pure, from the Yokozawa Chemicals Co.) and Y_2O_3 (99.9% pure, from the Johnson Matthey & Co., London). The carefully-mixed specimen was pressed into a $6\times6\times35$ mm bar under a pressure of 4000 kg/cm^2 and sintered at 1700°C for 3 hr with two heating and grinding cycles.

Results

The cooling-curve data are summarized in Fig. 1, while the mean values of from forty to fifty individual readings of the freezing point for each composition are indicated in Table 1. Anomalies in the liquidus curve not previously reported were found with compositions of 7.5, 15.0, and 20.0 mol% Y_2O_3.

In order to examine the stoichiometry of a composition quenched from the melt, the Y_2O_3 content of a specimen was analysed by chelate titration with an EDTA solution. The results obtained are shown in Table 2; the deviation from the stoichiometry was found to be almost negligible.

The findings on X-ray powder diffraction patterns of quenched specimens form the melt at the quenching rate of about 2000°C/sec are shown in Table 3. The Y_2O_3 solid solution was confirmed by means of diffraction lines from (332), (510), (541), and (631). The diffraction patterns of a 15 mol% Y_2O_3 composition quenched from the melt showed a broadening of peaks, though no extra reflection line was observed

1) P. Duwez, F. H. Brown, Jr., and F. Odell, *J. Electrochem. Soc.*, **98**, 356 (1951).

2) L. E. Olds and H. E. Otto, "Phase Diagram for Ceramists," ed. by E. M. Levin, C. R. Robbins and H. F. McMurdie, Amer. Ceram. Soc., Columbus, Ohio (1964).

3) Fan Fu-Kan, A. K. Kuznetsov and E. K. Keler, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, No. 7, 1141 (1962).

4) M. Foex and A. Rouanet, *C. R. Acad. Sci., Paris, Ser. C*, **264**, 947 (1967).

5) A. Rouanet, *ibid.*, **267**, 1581 (1968).

6) T. Noguchi, M. Mizuno and W. M. Conn, *J. Solar Energy*, **11**, 136 (1967).

7) T. Noguchi and M. Mizuno, This Bulletin, **41**, 1583 (1968).

8) T. Noguchi and T. Kozuka, *J. Solar Energy*, **10**, 125 (1966).

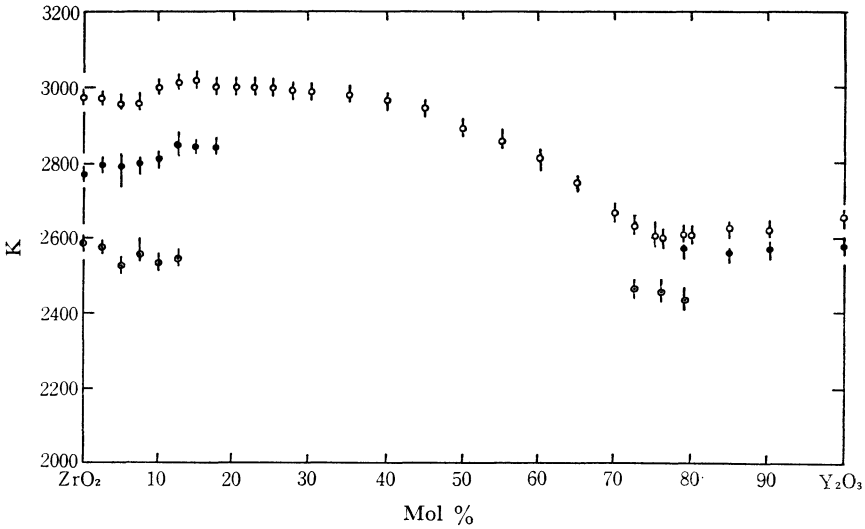

Fig. 1. Freezing point data in the ZrO_2-Y_2O_3 system.
○ Freezing point
● 2nd exothermic peak } (solid state)
⊙ 3rd exothermic peak }

Table 1. Freezing point data of ZrO_2-Y_2O_3 system

Composition ZrO_2 (mol%)	Composition Y_2O_3 (mol%)	Freezing point (±20°C)	Spectral emissivity at 0.65 μm
100		2706	0.81
97.5	2.5	2704	0.83
95	5	2690	0.88
92.5	7.5	2689	0.88
90	10	2728	0.89
87.5	12.5	2751	0.86
85	15	2746	0.89
80	20	2736	0.88
77.5	22.5	2735	0.87
75	25	2732	0.86
72.5	27.5	2720	0.88
70	30	2717	0.89
65	35	2708	0.90
60	40	2700	0.90
55	45	2675	0.89
50	50	2622	0.90
45	55	2592	0.89
40	60	2545	0.91
30	70	2449	0.89
25	75	2398	0.90
24	76	2330	0.92
20	80	2342	0.87
10	90	2351	0.87
	100	2376	0.96

through 2θ 160°. The high-temperature X-ray diffraction data for this specimen through 2θ 25°—38° up to 1350°C showed a cubic modification in both heating and cooling processes. The lattice

Table 2. Chemical analysis of quenched specimens from the melt in the ZrO_2-Y_2O_3 system

Sample	Y_2O_3 content (Theoretical) wt%	Y_2O_3 content (Determined) wt%	Y_2O_3 content (Determined) mol%	Difference mol%
Y 10	16.91	17.21	10.19	+0.19
Y 22.5	34.73	34.38	22.23	−0.27
Y 30	43.99	43.32	29.43	−0.57
Y 45	59.99	59.57	44.57	−0.43
Y 75	84.61	85.04	75.62	+0.62
Y 90	94.28	94.26	89.96	−0.04

Table 3. X-Ray diffraction data of quenched specimens from the melt in ZrO_2-Y_2O_3 system

Composition ZrO_2 (mol%)	Composition Y_2O_3 (mol%)	Phase present after quenching		
97.5	2.5	M (m)		
95	5	M (vw)	C*(m)	
92.5	7.5		C*(s)	
90	10		C*(s)	
85	15		C*(s)	
80	20		C (s)	
70	30		C (s)	
60	40		C (s)	
50	50		C (s)	
40	60		C (s)	Y (vw)
30	70		C (m)	Y (w)
25	75		C (w)	Y (m)
20	80			Y (s)
10	90			Y (s)

M: monoclinic zirconia solid solution; C: cubic zirconia solid solution; C* cubic not resolved; Y: yttria solid solution

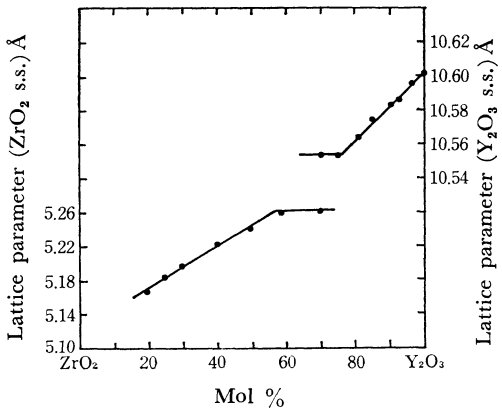

Fig. 2. Lattice parameters of cubic solid solutions.

parameters of the cubic zirconia solid solution were obtained at 2θ 1/8° from the diffraction lines with $2\theta > 90°$, and those of the yttria solid solution, with (332), (510), (541), and (631). The two-phase region containing a cubic zirconia solid solution and a yttria solid solution extended from 57—76 mol% Y_2O_3, as is shown in Fig. 2.

In a microscopic observation of the thin section of specimens quenched from the melt, the sample with a 15 mol% Y_2O_3 composition showed biaxial negative crystals with an optic angle of $2V = -80°$ unlike that of the monoclinic crystals ($-30°$), as in the cases of 7 mol% CaO and 12.5 mol% MgO compositions. The zirconia modification of this type is possibly of the rhombic form, though verification by X-ray diffraction data was not possible at present because of the difficulty in obtaining the single crystal.

These results suggest that the liquidus curve in the ZrO_2-rich side region of the ZrO_2-Y_2O_3 system is located at higher temperatures than those of ZrO_2-MgO and ZrO_2-CaO systems, as is shown in Fig. 3. An eutectic point on the yttria side was located at 76 mol% Y_2O_3 and at 2330°C. Further investigations should be focussed on the high-

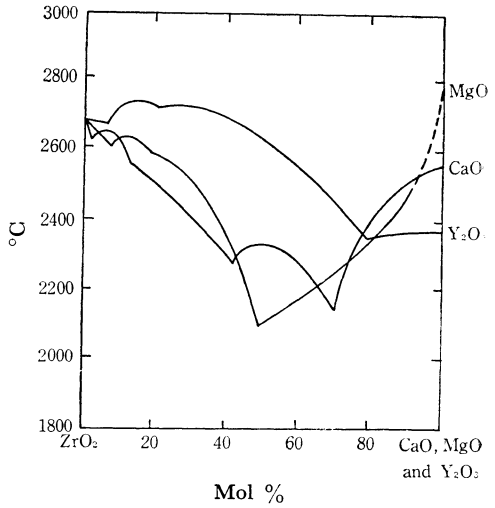

Fig. 3. Liquidus curves for binary oxide systems containing ZrO_2.

temperature phase study in the ZrO_2-rich side region in order to establish the complete phase diagram in the system.

Yttria showed its exothermic peak at about 2283°C in the solid state in the cooling curve; this might be ascribed to the cubic-hexagonal transition, as has been proposed by Rouanet.[5] However, the two phase-region of the cubic and hexagonal yttria solid solutions could not be clearly determined from the cooling-curve data.

The very narrow region for the monoclinic zirconia solid solution and the transformation of 15 mol% Y_2O_3 composition at a very high temperature might be assumed. The existence of the compound claimed by Fu-Kan *et al.* was not confirmed in this study.

The authors wish to express their appreciation to Dr. Hiroshi Hayashi for his help in the chemical analysis of the quenched specimen and in the microscopic work.