Solidus/Liquidus of UO_2-ZrO_2-Concrete Mixtures

Summary and Preliminary Recommendation

The preliminary recommendations for the solidus and liquidus temperatures of UO_2-ZrO_2-concrete mixtures are from differential thermal analysis (DTA) and viscosity measurements by Roche et al. [1]. The only other data reported in the open literature are solidus temperatures of basaltic and limestone concretes of unspecified composition [2] and solidus temperatures of mixtures of one of these concretes (limestone) with UO_2 and with UO_2-ZrO_2-FeO-Cr_2O_3 [2].

Roche et al. used DTA and rotational viscometry to measure solidus and liquidus temperatures of four concretes (limestone, limestone-common sand, siliceous, and basalt) and of their mixtures with urania and zirconia at a UO_2-to-ZrO_2 mole ratio of 1.6:1. The weight percent of concrete in these mixtures ranged from 10 to 100%. For limestone-sand concrete, data were also obtained for the UO_2-to-ZrO_2 mole ratio of 5:1. Severe corrosion of the crucible prevented precise determination of the liquidus temperature of basalt concrete and of UO_2-ZrO_2-basalt concrete mixtures. Data from the measurements of Roche et al. [1] are shown in Figure 1 and Table 1 as a function of weight percent of concrete in the mixture. The arrows on the liquidus temperatures in Figure 1 indicate that the temperatures are higher than these data. The data represent the highest temperature obtained in the experiments. Compositions of the concretes used in the measurements are given in Table 2.

Uncertainty

Roche et al. gave no estimate of the uncertainties of their results. However, they used the same DTA apparatus and technique to measure the melting point of NBS Standard Reference Material 742 (alumina), which has a melting point of 2326 $\pm$ 5 K. For this alumina standard, Roche et al. obtained the melting point of 2318 K. Thus, for this sample, the error experimental error was less than 1%. Because all the solidus temperatures determined by Roche et al.[1] were well within the limitations of their thermocouples and DTA apparatus, the solidus errors are estimated as $\pm$ 10% from the possible errors in temperature measurements with W/Re thermocouples. Errors in the liquidus temperatures for mixtures with limestone and limestone-common sand concretes are considerably larger because the liquidus temperatures for these mixtures could not be determined either by DTA or by viscosity measurements because of the temperature limitation of the resistance furnaces. In these cases, only a minimum is given for the liquidus temperature is given.

Discussion

DTA Measurements

Solidus and liquidus temperatures for mixtures of concrete and UO_2-ZrO_2 with the weight percent of concrete ranging from 10% to 100% were determined by Roche et al.[1] from differential thermal analysis (DTA) in a tungsten resistance furnace. The mole ratio of UO_2-to-ZrO_2 selected for most of the measurements was 1.6 : 1, a ratio that is typical of pressurized water reactors (PWR's) and that was used in large-scale molten core-concrete experiments at Argonne National Laboratory [3]. As the experiments progressed, the experimental technique was constantly improved to ensure good thermal measurements and to prevent loss of the sample by vaporization. Samples ranged in size from 10 to 20 g. Tungsten-rhenium theromcouples (W-25wt%Re vs W-3wt% Re) located in thermal wells in the molybedenum crucibles were used to measure the sample temperature and the reference (yttria) temperature. An NBS alumina standard (NBS Stamdard Reference Material 742) was used as a check of the sensitivity to thermal events. The measured melting point of the NBS alumina standard was 2318 K, in reasonable agreement with the stated melting point of 2326 $\pm$ 5 K. Vaporization losses were kept below 2% of the mass of the calcined concrete by doing the measurements in Ar-3% H_2 gas at pressures of 15 to 40 kPa. A special pretreatment procedure was adopted for DTA experiments with mixtures containing 10 wt% concrete because of concerns that (1) these samples would not melt sufficiently to provide good contact with the thermocouple because of their high liquidus temperature (>2500 ^oC) and (2) the samples, if not pretreated at a high temperature, would not contain equilibrium phases. Thererfore, these samples were heated for up to an hour under flowing Ar-3%H_2 (at 15 kPa) at temperatures as high as 2500 ^oC for limstone-concrete and 2200 ^oC for siliceous concrete.

The DTA measurements produced a series of heating and cooling curves at various heating rates (10 to 50^{o}C/min). Solidus temperatures were determined from the first event detected in the heating curves. Liquidus temperatures were determined from the first event detected in the cooling curves. DTA measurements also provided information on the type of crystallization. Forms of crystallization observed in these measurements included formation of eutectics, crystallization of multiple phases at different temperatures, and glass formation. A sharp peak in the DTA curves at the solidus temperature indicated a eutectic. Multiple peaks in the liquidus-solidus temperature range indicated that a number of phases crystallized at different temperatures.

Roche et al. [1] also conducted DTA measurements on mixtures of urania and calcia to redetermine the CaO-UO_2 phase diagram because earlier phase diagrams did not agree. The CaO-UO_2 phase diagram is needed by computer programs [4,5] that calculate solidus and liquidus temperatures of core-concrete mixtures from phase diagrams of simpler systems.

Viscosity Measurements

Roche et al. [1] used rotational viscometry to estimate some liquidus temperatures of UO_2-ZrO_2-concrete mixtures because higher temperatures (2850 K vs 2675 K) could be obtained via viscometry, which did not require continuous operation of a thermocouple. However, the viscometry measurements lacked the high precision of DTA and could be used only to determine the liquidus temperature, not the solidus temperature. The rotational viscometry measurements were done with a programmable Brookfield viscometer that detected the torque required to rotate a cylindrical spindle in the urania-zirconia-concrete mixtures as a function of spindle rpm (rotations per minute). Below the liquidus temperature, the mixtures exhibited both a high viscosity and a high degree of shear thinning. Above the liquidus temperature, the completely liquid mixtures showed Newtonian behavior, i.e. the viscosities were independent of the shear rate (the rate of spindle rotation) and the viscosities were much lower than that of the solid-liquid mixtures. Thus, the liquidus temperature was determined from the change in flow characteristics of the mixture from high viscosity and non-Newtonian behavior below the liquidus to low viscosity and Newtonian behavior above the liquidus.

The spindles used in these viscosity measurements were made from a 70 wt% molybdenum-30wt% tungsten alloy (70Mo-30W). The spindles were calibrated with Brookfield standard silicone fluids prior to use in the experiments. Core-concrete sample masses ranged from 150 to 200 g with volumes of approximately 30 cm^3. They were heated to 2850 K in the bottom of a 70Mo-30W furnace tube that was continuously purged by Ar-3% H_2 to keep the urania in the U^{+4} state. A tungsten resistance furnace was used for these measurements. Experiments were done at the highest temperature and repeated reducing the temperature in steps of 50 to 100 K until the mixture became too thick for viscosity measurements.

Discussion of Data

Table 1 shows the results of these measurements for each type of concrete and weight percent of concrete in the UO_2-ZrO_2-concrete mixtures. The mole ratio of UO_2-to-ZrO_2 and method of measurement have also been included in Table 1. The data for a urania- to- zirconia mole ratio of 1.6:1 are shown in Figure 1. The values in Figure 1 for UO_2-ZrO_2-0 wt% concrete are from the published UO_2-ZrO_2 phase diagram [6]. The arrows on the liquidus temperatures in Figure 1 indicate that the liquidus temperatures are higher than these data. The solidus/liquidus curves in Figure 1 have been proposed by Roche et al. [1] based on their data for the mixtures with the three concretes. These curves were not calculated from a theoretical model and are limited by the 2850 K temperature-limit of their experimental measurements. The differences between the solidus and liquidus temperatures shown in Figure 1 are hundreds of degrees greater than expected from calculations based on ideal-solution models.

Limestone Concrete

The heating curves from DTA measurements on limestone concrete showed three broad peaks centered at approximately 1500, 1900 and 2250°C. The solidus temperature, 1222°C (1495 K) was taken as the onset of the first peak in the 10°C/min heating curve. The liquidus temperature, 2304 °C (2577 K), was taken from the first break in the 10°C/min cooling curve. Roche et al. identified two narrow peaks at ~1565°C and ~1220°C as quarternary piercing points in ternary sections of the CaO-MgO-Al_2O_3-SiO_2 phase diagram. Three broad peaks in the cooling curve were identified with melting and crystallization of separate phases such as CaO, Ca_2SiO_4, and Melilite. After calcining to remove CO_2 and H_2O, the limestone concrete composition (shown in Table 2) may be approximated as 71 wt% CaO, 12 wt% SiO_2, 12 wt% MgO and 5 wt% other oxides (mainly Al_2O_3). From examination of ternary sections of quaternary phase diagrams of these oxides [7,8], Roche et al. [1] concluded that the solidus-liquidus temperature range for this mixture should be approximately 1235°C to 2250°C (1508 to 2523 K). This range is consistent with the 1222°C to

2304°C (1495 to 2577 K) range obtained by Roche et al. from DTA measurements.

Mixtures of UO_2, ZrO_2 and Limestone Concrete

Solidus temperatures for 60, 27.5, and 10 wt% concrete were obtained from the first break in the DTA heating curves for these mixtures. However, cooling curves provided no information on the liquidus temperature for these mixtures because the thermocouples failed above 2400°C (~2670 K). Examination of phase diagrams for the CaO-UO_2 and CaO-ZrO_2 systems indicate that the liquidus temperature for a UO_2-ZrO_2 (1.6:1 mole ratio) mixture with 27.5 wt% limestone concrete would be greater than 2450°C (2723 K). The main feature in the curves for 10 wt% concrete is the peak from about 1950 to 2000°C (~2220 to 2270 K) that corresponds to melting the calcia-urania-zirconia phase. The CaO-UO2 eutectic is 1945°C (2218 K).

Viscosity measurements using 70Mo-30W spindles were made with samples containing 60, 36.2, and 27.5 wt% limestone concrete. At 2577°C (2850 K) the mixtures exhibited non-Newtonian behavior with viscosities above 1 Pa s indicative of the presence of a solid phase. Thus, the liquidus temperatures for these mixtures is much greater than 2850 K.

Limestone-Sand Concrete

The solidus and liquidus temperatures for limestone-sand concrete obtained by Roche et al. [1] from DTA measurements on three separate samples are shown in Table 1. Because the composition of the calcined limestone-sand concrete, given in Table 2, may be approximated as 37 wt% CaO, 40 wt% SiO_2, 13 wt% MgO, 7 wt% Al_2O_3 (combining Al_2O_3 and Fe_2O_3) and 3 wt% other species (mainly Na_2O), Roche et al. [1] compared the results of these measurements with ternary sections of the quinary system Na_2O-CaO-MgO-Al_2O_3-SiO_2, which has been studied in detail [7]. These sections indicate that the solidus-liquidus temperature range of 1120 to 1295°C (1393 to 1568 K) is reasonable for concrete with this approximate composition.

Mixtures of UO_2, ZrO_2 and Limestone-Sand Concrete

Solidus temperatures obtained from DTA measurements of mixtures of urania and zirconia with 80, 47, 27.5, and 10 wt% limestone-sand concrete are shown in Table 1. The urania-to-zirconia mole ratio was 1.6:1 for samples containing 80, 27.5, and 10 wt% concrete. It was 5:1 in the sample containing 47 wt% concrete. The different mole ratio was selected for this sample in order to study the effect of urania-to-zirconia ratio on the liquidus temperatures. The solidus temperatures are mainly dependent on the concrete and would not be expected to be significantly effected by the urania-to-zirconia mole ratio. Because the liquidus temperature was above the 2400°C (~2670 K) temperature limit of the apparatus, Roche et al. concluded that the effect, if any, of urania-to-zirconia ratio on liquidus temperatures would be undetectable in their DTA apparatus. The liquidus temperature for the sample containing containing 27.5 wt% concrete is given in Table 1 as greater than 2365°C (2638 K) from detection on cooling of a broad peak, which was centered at 2150°C and extended to ~ 2000°C. The onset of this peak, which is associated with the crystallization of a UO_2-ZrO_2-CaO solid solution, is above 2365°C (2638 K). Although minor peaks were observed in the cooling curve of the 80 wt% sample, a liquidus temperature could not be extracted from the curves. The DTA heating and cooling curves for the sample containing only 10 wt% limestone-sand concrete were very similar to those for the sample with 10 wt% limestone concrete. No liquidus temperature could be determined for this sample.

Viscosity measurements to determine the liquidus temperature were made on the sample containing 27.5 wt% concrete and on a sample containing 60.4 wt% concrete with a urania-to-zirconia mole ratio of 5:1. At the highest temperature (2577^oC), non-Newtonian behavior was observed for both samples indicating the presence of solid-liquid mixtures.

Siliceous Concrete

No crystallization peaks were observed from DTA measurements on siliceous concrete but a glass transition from 1130 to 1250 ^oC (1403 to 1523 K) was detected by Roche et al.[1]. The onset of this glass transition at 1130^oC is consistent with a softening temperature at ~ 1140^oC that was reported by Skokan et al. [2] for siliceous concrete. Skokan et al. commented that because this concrete solidifies into a glass, the softening temperature is more relevant than the thermodynamic crystallization temperature. Based on the composition of this concrete given in Table 2, a calcined sample of this concrete could be approximated by 15 wt% CaO, 77 wt% SiO_2, and 8 wt% of other oxides (mainly Al_2O_3). From the CaO-Al_2O_3-SiO_2 ternary diagram, Roche et al. estimated the solidus as 1170^oC and the liquidus as 1520^oC. Thus, the glass transition temperature range reported by Roche et al. occurs over a smaller temperature range than the equilibrium temperature range (1170-1520^oC).

Mixtures of UO_2, ZrO_2 and Siliceous Concrete

DTA measurements were made on samples that contained 100, 80, 27.5, and 10 wt%siliceous concrete. The urania-to-zirconia mole ratio was 1.6 to 1 in all mixtures with siliceous concrete. For 80 wt% siliceous concrete,the steep slope in the heating and cooling curves at both high and low temperatures prevented detection of a glass transition that could have been expected in the 1100 - 1300^oC temperature range. Roche et al. tentatively selected 2170^oC (2443 K) for the liquidus of this mixture based on the onset of peaks at this temperature. The glass transition from 1134 to 1322 ^oC (1407 - 1595 K) that was detected in the heating curve of the sample with 27.5 wt% concrete is consistent with the 100 wt% concrete sample. The liquidus temperature for the 27.5 wt% concrete, 2276^oC (2549 K) reported by Roche et al. from a minor peak in the cooling curve appears reasonable when compared to liquidus temperatures in the binary systems for SiO_2-UO_2 and SiO_2-ZO_2. A UO_2-ZrO_2 phase and a silicate phase were detected in cooled mixtures of UO_2, ZrO_2, and siliceous concrete in large-scale molten core-concrete interaction experiments [3] and in small-scale vaporization experiments [9]. The DTA heating and cooling curves for the sample that contained 10 wt% siliceous concrete are similar to those for 10 wt% limestone concrete and 10 wt% limestone-sand concrete. The solidus temperature, 1610^oC (1883 K) was selected from the onset of a broad shallow peak that extended to above 1750^oC (2023 K). No liquidus temperature was determined for this sample.

Basalt Concrete

The DTA curves for the basalt concrete sample showed a glass transition over the temperature range of 900 to 1100°C (1173 to 1373 K). X-ray diffraction examination of the solidified sample indicated it was amorphous.

Mixtures of UO_2, ZrO_2 and Basalt Concrete

Because of severe corrosion problems in the DTA measurement on a mixture of urania and zirconia (1.6 to 1 mole ratio) with 27.5 wt% basalt concrete, no additional measurements were attempted. A glass transition in the range of 900 to 1200°C (1173 to 1473 K) was detected from the DTA curves for the sample containing 27.5 wt% basalt concrete. Complex peaks in the temperature range of 2100 to 2400°C could not be confidently interpreted by Roche et al.[1] because at high temperature, the sample corroded through the wall of the molybdenum crucible so that only 17% of the mass remained in the crucible at the end of the experiment. Roche et al. reported that the most likely reaction to cause this corrosion in the reducing atmosphere in the furnace was a reaction between the molybdenum and the iron oxide component of the basalt concrete. From the corrosion, Roche et al. concluded that under reactor accident conditions, the iron oxide in basalt concrete would probably be reduced so that core-concrete mixtures with basalt concretes would be quite close in composition to core-concrete mixtures with siliceous concrete.

Comparison of Data with Calculations

Solidus and liquidus temperatures for mixtures with siliceous concrete measured by Roch et al. [1] are in reasonable agreement with thermodynamic calculations [4,5]. Liquidus temperatures for some mixtures with limestone-sand or limestone concrete were 300-500°C higher than the thermodynamic calculations. Roche et al. state that agreement between measurements and calculations should improve when the results of their new CaO-UO_2 phase diagram study have been incorporated into the thermodynamic calculations, which currently use an unusually low eutectic temperature of 1850°C (2123 K) proposed by Holc and Kolar [10] for CaO-UO_2.

References

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Table 1 Solidus and Liquidus Temperatures of UO_2-ZrO_2-Concrete Mixtures

Concrete Type	wt% Concrete	UO_2 : ZrO_2 Mole Ratio	Temperature, K		Measurement Method
			Solidus	Liquidus	
Limestone	100	-	1495	2577	DTA
	60	1.6 : 1	1573 -	N.D.* > 2850	DTA Viscometry
	36	1.6 : 1	-	> 2850	Viscometry
	27.5	1.6 : 1	1520 -	> 2723 > > 2850	DTA Viscometry
	10	1.6 : 1	1888	-	DTA
Limestone-Sand	100	-	1393	1568	DTA
	80	1.6 : 1	1518	-	DTA
	60.4	5 : 1	-	> 2850	Viscometry
	47	5 : 1	1448	>2723	DTA
	27.5	1.6 : 1	1360 -	>2638 >2850	DTA Viscometry
	10	1.6 : 1	1848	-	DTA
Siliceous	100	-	1403 - 1523**	-	DTA
	80	1.6 : 1	-	2443	DTA
	27.5	1.6 : 1	1407 - 1595** -	2549 >2367	DTA Viscometry
	10	1.6 : 1	1883	-	DTA
Basalt	100	-	~ 1173 - 1373**		DTA
	27.5	1.6 : 1	~ 1173 - 1473**	> 2500†	DTA

* N. D. = Not detected in two separate experiments;
** Glass-transition temperature range;
† Severe crucible corrosion prevented a precise determination.

Table 2 Composition of Concretes (in Weight Percent) from Chemical Analysis

Species	Concrete Composition, wt%			
	Limestone Concrete	Limestone-Sand Concrete	Siliceous Concrete	Basalt Concrete
Na_2O	0.034	1.09	0.69	3.06
K_2O	0.40	0.57	1.41	1.41
MgO	7.44	9.62	0.70	3.03
CaO	42.96	26.02	13.47	12.51
SrO	0.030	0.031	0.023	0.046
BaO	0.007	0.032	0.021	0.07
Al_2O_3	1.91	3.48	4.04	11.26
SiO_2	7.13	28.27	68.99	52.80
TiO_2	0.097	0.143	0.81	1.35
V_2O_5	0.011	0.012	0.000	0.045
Cr_2O_3	0.006	0.009	0.007	0.016
MnO	0.014	0.054	0.028	0.137
Fe_2O_3	0.80	1.64	1.00	8.58
CoO	0.003	0.003	0.000	0.006
NiO	0.004	0.005	0.000	0.006
CuO	0.011	0.005	0.000	0.008
ZnO	0.005	0.007	0.000	0.024
ZrO_2	0.004	0.019	0.000	0.026
$CO_2 + H_2O$	40.64	27.54	7.91	4.36
(CO_2)	(33.63)	(21.41)	(4.23)	
Sum:	101.5	98.6	99.1	98.7

Figure 1 Solidus-Liquidus Temperatures for UO_2-ZrO_2-Concrete Mixtures