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The eutectic and liquidus in the Al_2O_3–ZrO_2 system

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A high-temperature X-ray diffraction method was employed to establish, *in situ*, the eutectic temperature (1910 ± 20° C) and the liquidus line in the Al_2O_3–ZrO_2 binary system. The eutectic composition was determined by optical microscopy to be 42.5 ± 1 wt % ZrO_2. No evidence was found for the existence of a reported ϵ-Al_2O_3 high temperature phase.

1. Introduction

The Al_2O_3–ZrO_2 phase diagram has been the subject of scientific study for quite a number of years. These two oxides are of interest because they are highly corrosion resistant and refractory, and they are common constituents in glass contact refractories.

The earliest paper on the Al_2O_3–ZrO_2 phase diagram, generally referenced in the literature, was published in Germany in 1928 by von Wartenberg *et al.* [1] who studied various highly refractory oxides. During their work von Wartenberg *et al.* examined powder mixtures of Al_2O_3 and ZrO_2 with the Al_2O_3 content increasing in steps of 10 wt% and pre-fired at 1700° C. Depending on the composition of the specimens, either the softening or the melting points were determined. No evidence for the formation of any ortho- or metazirconates was found. The eutectic temperature of the Al_2O_3–ZrO_2 system was ascertained as 1920° C, and the melting point of pure Al_2O_3 as 2055° C.

Dietzel and Tober [2, 3] reported in 1953 on their investigations of almost 30 binary systems of various oxides and ZrO_2. Their work is particularly noteworthy because it was one of the first *in situ* studies of phase diagrams by a high-temperature X-ray diffractometry. They do not specifically describe any results on the Al_2O_3–ZrO_2 system, probably because the temperatures of interest in that system are above the capabilities of their Pt–Rh heater material. The authors discuss, however, the ZrO_2 single phase system and come interestingly enough to the conclusion that cubic ZrO_2 is formed only if certain other oxides are present.

Suzuki *et al.* [4] published their work on the Al_2O_3–ZrO_2 phase diagram in 1961. A eutectic temperature of 1890 ± 5° C was determined for a eutectic composition of 45 wt% Al_2O_3–55 wt% ZrO_2. In 1965 Krauth and Meyer [5] described their findings on quenched modifications and crystallite growth in ZrO_2 systems. For the Al_2O_3–ZrO_2 system they reported a eutectic composition of 65.9 wt% Al_2O_3 and 34.1 wt% ZrO_2.

Cevales [6] published a new phase diagram for Al_2O_3–ZrO_2 in 1968 and reported the discovery of a new high temperature phase in the system which he named ϵ-Al_2O_3. He found a eutectic temperature of 1710 ± 10° C for a composition of 54.7 wt% Al_2O_3 and 42.6 wt% ZrO_2. His work was in part carried out on samples heated in a high-temperature X-ray diffraction camera capable of $\geqslant$ 1930° C, and in part on quenched samples. The new ϵ-Al_2O_3 phase which he described could be indexed hexagonally with $a = 7.849$ Å and $c = 16.183$ Å and was formed at temperatures above 1930° C and in compositions of about 1 wt% ZrO_2.

Schmid and Viechnicki [7] studied oriented eutectic microstructures in the Al_2O_3–ZrO_2 system and reported a eutectic temperature of 1870 ± 5° C at 58.5 wt% Al_2O_3 and 41.5 wt% ZrO_2. The Al_2O_3–ZrO_2 system was studied in the late 1960s by optical microscopy of the microstructure and X-ray diffraction of quenched specimens

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TABLE I Literature values for the eutectic temperature and composition in the Al_2O_3–ZrO_2 phase diagram

Reference	Eutectic temperaure (°C)	Eutectic composition	
		(wt % ZrO_2)	(mol % ZrO_2)
von Wartenberg *et al.* [1]	1920 ± 10	–	–
Suzuki *et al.* [4]	1890 ± 5	~ 55	~ 50.3
Krauth and Meyer [5]	–	34	30
Cervales [6]	1710 ± 10	42.6	38.1
Schmid and Viechnicki [7]	1870 ± 5	41.5	37.0
Alper *et al.* [8]	1900	~ 41	36

by Alper *et al.* [8]. These workers determined a eutectic temperature of 1900° C for a eutectic composition of about 60 wt% Al_2O_3 and 40 wt% ZrO_2. The experimental method used is described in detail by McNally *et al.* [9].

The brief literature survey of the Al_2O_3–ZrO_2 system presented here clearly indicates that the results quoted by various workers and summarized in Table I vary widely. The spread in the eutectic temperatures reported is more than 200° C, ranging from a low value of 1710 to 1920° C. The eutectic compositions reported range from about 34 to 55 wt % ZrO_2.

In view of these rather large discrepancies in the various Al_2O_3–ZrO_2 phase diagrams reported, it was decided to attempt to establish the phase diagram more reliably. This decision was encouraged by the fact that the intended studies could be made utilizing an *in situ* method, namely, a newly developed high-temperature X-ray diffractometer technique capable of the rather high sample temperatures required. The work carried out and reported here consists of the determination of the eutectic composition and temperature, and the establishment of the liquidus line in the system. Also brief attempts were made to synthesize the ϵ-Al_2O_3 phase reported by Cevales [6].

2. Experimental procedure

2.1. Sample preparation

The samples used in the current study of Al_2O_3–ZrO_2 system were prepared by co-precipitation of Al- and Zr-hydroxides from the respective chlorides, using ammonium hydroxide. The resulting gels were further mixed, air dried and subsequently calcined at 1000° C for 1 h in order to assure the removal of all remaining chlorine, ammonia and water. The resulting fine powders were very homogeneous and highly reactive. Each batch prepared was chemically analysed to determine the Al_2O_3 and ZrO_2 contents.

The chemical analyses for both of the elements of interest were carried out by two different methods. The Al_2O_3 content was determined by complexometric titration and atomic absorption, and the ZrO_2 content by complexometric and gravimetric techniques. The absolute error in the ZrO_2 content analysed is ± 1% for specimens of $\geqslant 90$ wt% ZrO_2, and the relative error for lower weight percentages of ZrO_2 is $\leqslant 0.5$ wt%; furthermore, the reported ZrO_2 values include a relative 1.8 wt% hafnia. A semiquantitative spectrographic analysis of all specimens for trace impurities was also performed. Four representative results of the impurity analysis are included in Table II.

The samples for the determination of the eutectic composition by optical microscopy examination of the microstructure were prepared from carefully weighed mixtures of reagent grade Al_2O_3 and ZrO_2 powders. The powder mixtures were pressed into pills and stacked so that the top two pills were in the hot zone of an induction furnace. The samples were heated in argon until the top pills melted. Polished sections were prepared for the microscopy work.

The sample preparation for the X-ray diffrac-

TABLE II Trace impurities (ppm)

ZrO_2 (wt %)	Fe	Pb	Cu	Ba	Si
8.8 ± 0.04	300–1000	100–300	< 100	–	< 100
36.8 ± 0.2	100–300	< 100	–	–	< 100
82.8 ± 0.4	100–300	–	–	< 100	< 100
97.5 ± 1.0	100–300	–	–	100 – 300	< 100

No detectable chlorine in any of the samples.

tion studies consisted of grinding the fired $Al_2O_3-ZrO_2$ materials to a 325 mesh powder for packing into the sample holders and/or 0.3 mm glass capillaries. Xylene was used to prepare slurries that were applied to the Ta heater substrates. This latter procedure resulted in samples of random orientation, of a surface smooth enough for X-ray diffractometer work and of easily controllable sample size. The sample films were about six millimeters in diameter and consisted of approximately 0.05 g of sample, the minimum amount required to produce a detectable X-ray signal.

2.2. Instrumental details

The room-temperature powder X-ray diffraction work for the examination and identification of precursor materials and of samples quenched after firing was carried out on a Norelco-Canberra generator–detector panel combination with a vertical Norelco wide angle goniometer. The X-ray diffraction traces were strip-chart recorded using reflected-beam monochromatized copper ratiation.

Additional Debye–Scherrer film diagrams were occasionally recorded as needed on a 57.3 mm power camera with Ni-filtered copper ratiation.

The high-temperature powder X-ray diffraction work was performed on a Norelco generator with a vertical Norelco wide-angle goniometer and a Hamner detector panel with a Honeywell strip-chart recorder. Ni-filtered copper ratiation was employed. The specimens were heated in a Materials Research Corporation (MRC) high temperature diffractometer attachment which was slightly modified to achieve the necessary very high temperatures.

The sample holders for the MRC attachment are of the substrate heater type and can be shaped from various refractory metals, depending on the temperature range desired. Tantalum foil of 5 mm thickness was used in this study. A helium atmosphere thoroughly freed from any traces of O_2 was maintained in the sample chamber to prevent the oxidation of the carefully cleaned sample holders.

Very good temperature stability was maintained at all times during the experiments, and lateral and vertical temperature gradients in the sample were negligible because of the small sample size.

The sample temperatures were determined by matching the apparent brightness of the Ta sample holder with the brightness of the pyrometer filament. These pyrometer readings were converted into the correct sample temperatures with the help of calibration curves established from well known melting points. Table III lists the melting points used to establish the calibration curves needed for various angles of reflection. The estimated accuracy of temperature measurement using this procedure is ± 20° C, and the precision is better than ± 10° C.

The determination of the eutectic and liquidus temperatures as functions of sample composition was carried out *in situ*, i.e. by high-temperature X-ray diffraction. Samples were heated on the Ta substrate heater to the desired temperatures and selected X-ray reflections monitored by strip-chart recording. The sample temperatures were systematically increased until the disappearance of the reflected X-ray peak indicated melting of the specimen. Several successive high temperature runs were made on each composition, and the results of these runs averaged to yield the correct melting temperature.

3. Results and discussion

The microscopic analysis of fused samples proved the eutectic composition to be 42.5% ± 1% ZrO_2 by weight. This can be clearly seen in Fig. 1. The composition containing 44 wt % ZrO_2 (a) possesses primary zirconia phase, and the eutectic phase indicating that the sample is on the ZrO_2 side of the eutectic. On the other hand, the sample containing 41 wt % ZrO_2 (d) possesses primary alumina in its microstructure and is, therefore, on the Al_2O_3 side of the eutectic. Samples in between show only the eutectic microstructure. This result is in agreement with the results of Cevales [6], Schmid and Viechnicki [7] and Alper *et al.* [8].

The eutectic temperature found by the high-temperature X-ray technique for the $Al_2O_3-ZrO_2$ system is 1910 ± 20° C. This temperature is in excellent agreement with the value of 1900° C determined by Alper *et al.* [8] and, interestingly enough, with the 1928 results of von Wartenberg

TABLE III Melting points used for temperature calibration curves

Substance	Temperature (°C)
Gold	1064*
Platinum	1772†
Corundum (α-Al_2O_3)	2044‡
Zirconia (ZrO_2)	2710§

* Fixed point of IPTS 1968.

† Secondary reference point of IPTS 1968.

‡ See Charlesworth [10].

§ See Charlesworth [11].

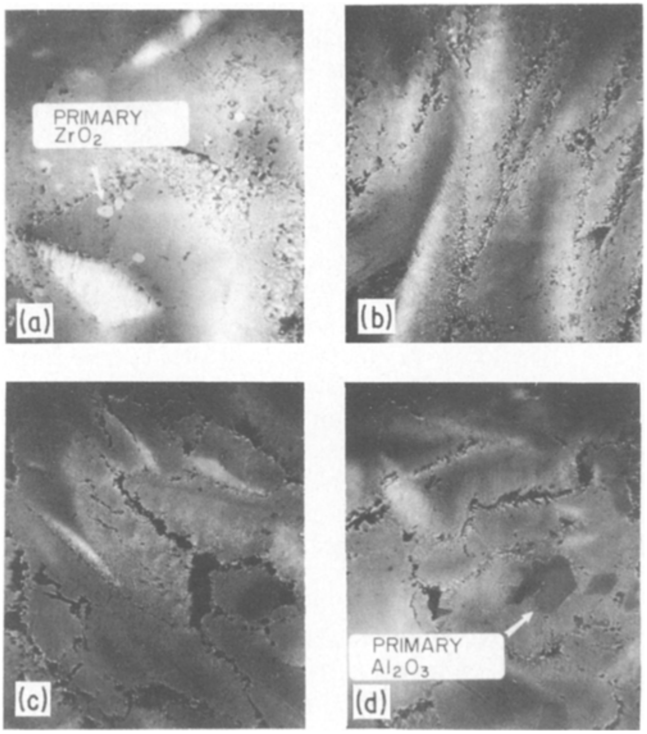

Figure 1 Typical microstructures of melted samples of Al_2O_3 plus ZrO_2 near the eutectic composition (400 X). (a) 44 wt% ZrO_2, (b) 43 wt% ZrO_2, (c) 42 wt% ZrO_2 and (d) 41 wt% ZrO_2.

et al. [1] (1920 ± 10° C). Suzuki *et al.* [4], who reported 1890 ± 5° C, are also reasonably close to this result. All other literature values are rather different, especially the 1710° C reported by Cevales [6]. The latter value, particularly, is so low that normal instrumental and/or temperature reading uncertainties cannot account for the large discrepancy in the two determinations.

TABLE IV Liquidus temperature in the Al_2O_3–ZrO_2 system

Composition (wt % ZrO_2)	Temperature (°C)
(0)*	(2044)
8.8	2013
13.3	2014
23.4	1978
26.1	1999
36.8	1966
38.5	1962
39.1	1967
39.6	1940
42.5	1910
47.2	1930
58.6	1975
70.4	2155
76.7	2335
82.8	2380
88.7	2425
92.6	2545
95.0	2478
95.2	2654
97.5	2631
(100)	(2710)

* Figures in parentheses are literature values.

The liquidus line in the Al_2O_3–ZrO_2 system was established in two sections, namely, for composition of lower and of higher than eutectic ZrO_2 content and the disappearance of Al_2O_3 or ZrO_2 reflections was monitored, respectively. The melting points were again derived as the averages of

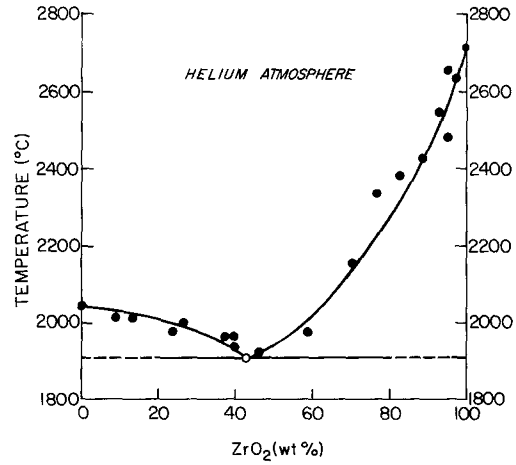

Figure 2 The eutectic and liquidus lines of the Al_2O_3–ZrO_2 equilibrium diagram determined by high-temperature X-ray analysis.

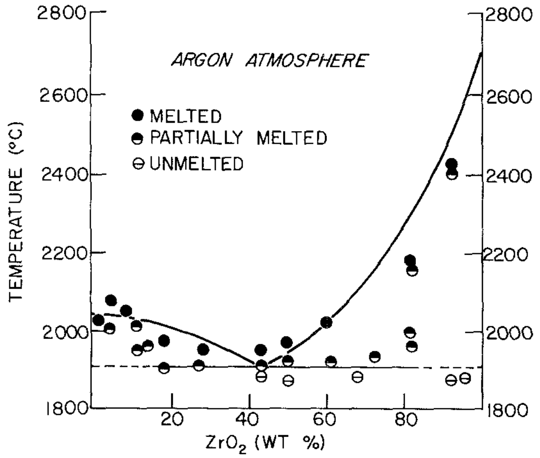

Figure 3 A comparison of the eutectic and liquidus lines determined by X-ray analysis with the observations of Alper *et al.* [8].

several consecutive high-temperature runs of a given composition, as described above.

The temperatures at which melting was observed as a function of wt% ZrO_2 are summarized in Table IV and the liquidus curve thus determined is plotted in Fig. 2. There is some evidence that there is a minor amount of solid solution between Al_2O_3 and ZrO_2, but this is not indicated in Fig. 2. To do so without further study would be pure guess-work. Fig. 3 is a reproduction of the curve in Fig. 2 but using the data of Alper *et al.* [8]. The figure demonstrates the good agreement between the data measured by *in situ* X-ray analysis and by conventional quenching techniques.

A number of attempts were made to confirm the presence of the ϵ-Al_2O_3 high temperature phase reported by Cevales [6]. Several samples with compositions of around 1 wt% ZrO_2 were prepared and heated in the high-temperature X-ray diffraction attachment. No evidence of the presence of that phase in our materials was found in the X-ray traces recorded immediately after heating and/or after various hold times. Cevales [6] reported that the lines of the new phase were more easily identified in the X-ray traces of quenched specimens than in the X-ray patterns recorded while being heated. Therefore, specimens were fired in a furnace to several temperatures around and above 1930° C and quenched after various lengths of time, but, again, no evidence was found for the new phase.

4. Summary

Large discrepancies between the Al_2O_3–ZrO_2 phase diagrams reported by various authors prompted this investigation of the eutectic and liquidus lines in the system.

The eutectic composition was determined to be 42.5 ± 1 wt% ZrO_2, and the eutectic temperature was found to be 1910 ± 20° C. The latter value and the liquidus line, including the ZrO_2-rich end, were determined *in situ* by a high-temperature X-ray diffraction method. The results of our study are in excellent agreement with the results of Alper *et al.* [8], who studied the phase diagram earlier by optical microscopy and X-ray diffraction of quenched specimens.

No evidence was found in our study for the existence of the high temperature phase ϵ-Al_2O_3 reported in the literature.

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References

1. VON H. V. WARTENBERG, H. LINDE and R. JUNG, *Z. Anorg. Allg. Chemie.* **176** (1928) 349.
2. VON A. DIETZEL and H. TOBER, *Ber. Dtsch. Keram. Ges.* **30** (1953) 47.
3. *Idem, ibid.* **30** (1953) 71.
4. H. SUZUKI, S. KUMURA, H. YAMADA and T. YAMAUCHI, *J. Ceram Assoc. Japan* **69** **(2)** (1961) 52.
5. VON A. KRAUTH and H. MEYER, *Ber. Dtsch. Keram. Ges.* **42** **(3)** (1965) 61.
6. VON G. CEVALES, *ibid.* **45** **(5)** (1968) 216.
7. F. SCHMID and D. VIECHNICKI, *J. Mater. Sci.* **5** (1970) 470.
8. A. M. ALPER, R. C. DOMAN, R. M. MCNALLY and H. C. YEH, in "Phase Diagrams" edited by A. M. Alper, (Academic Press, London and New York, 1970) p. 117.
9. R. N. MCNALLY, F. I. PETERS and P. H. RIBBE, *J. Amer. Ceram. Soc.* **44** (1961) 491.
10. J. H. CHARLESWORTH, "Melting Points of Metallic Elements and Selected Compounds", technical report ARML-TR-70-137 (1970) p. 71.
11. J. H. CHARLESWORTH, *ibid.* pp. 102–3.

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