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Phase diagram of the system: Al_2O_3–ZrO_2

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Abstract

The system Al_2O_3–ZrO_2 was studied by differential thermal analysis in inert atmosphere and in vacuum. The eutectic was located at 1866°C and 40% mass of ZrO_2. Zirconia solid solution at the eutectic temperature is up to 1.1±0.3% mass of Al_2O_3. Enthalpy of melting of this eutectic is 1080±90 J/g. Pure ZrO_2 transforms from monoclinic to tetragonal at 1162±7°C, but the saturated solid solution of ZrO_2, with 0.7±0.2% mass Al_2O_3 at this temperature, transforms at 1085±5°C. Inverse transitions occur with hysteresis correspondingly at 1055±5 and 995±5°C. Enthalpy of transformation of pure ZrO_2 from monoclinic to tetragonal phase is 42±5 J/g (5.2±0.6 J/mol) but only 30±5 J/g for a ZrO_2 saturated solid solution.

Keywords: C. Thermal properties; D. Al_2O_3; D. ZrO_2

The ZrO_2–Al_2O_3 oxide system is the basis of many advanced high temperature materials and refractories. The phase diagram of this system was studied by differential thermal analysis in the temperature range up to 2200°C within the composition interval from 0 to 100% mass ZrO_2. Samples were prepared from calcined oxides with more than 99.5% purity of main substance. Experiments were made in molybdenum crucibles in argon atmosphere as well as in vacuum (2–10×10^{-3} mm Hg) using a high temperature differential thermal analyser with three-crucible cell. The third crucible contains pure alumina that permits calibration of the thermocouple (tungsten rhenium 5/20) in situ by melting of Al_2O_3 at the same time as measurement of the sample in the neighbour crucible. The method, in combination with heating rate variation, has an accuracy of temperature determination better than ±10°C at 1700–2100°C. Heating rates were 10, 20, 60 and 100°C/min. Every sample (30–80 mg) was heated 3–5 times up to 2080–2200°C. All signals were carried through low noise amplifier, then converted by 15-bit analog–digital device and stored on hard disk drive.

The liquidus line clearly determined the temperature and composition of eutectic point: 1866±7°C and 40±1% mass ZrO_2 (Fig. 1). The broad region of liquid state 30–50°C above the eutectic point and similar coordinates of this point were reported earlier [1-4] but are unlike those of [5]. The heat effects of melting of eutectic as a function of composition are shown on Fig. 2. From this graph two conclusions were derived. First, the enthalpy of eutectic fusion is 1080±90 J/g. This value appears to be intermediate between those of pure alumina (1100±10 J/g) and pure zirconia (720±10 J/g) [6]. Second, the components dissolve in each other in the solid state. The width of solid solution (SS) in ZrO_2 at the eutectic temperature was estimated to be 8±2% mass Al_2O_3 and width of SS in Al_2O_3 is 3±2% mass ZrO_2, however further investigation demonstrates that it was too crude an estimation.

X-ray fluorescence microanalysis shows that, annealed at 900–1000°C, ZrO_2 SS contains 0.7±0.2% mass Al_2O_3 and the Al_2O_3 SS contains less than 0.01% mass ZrO_2. The first value is greater than reported earlier (<0.1% mass Al_2O_3 [7,8]) but the second value is in good agreement with other authors. The ZrO_2 partition in sample with 5% mass ZrO_2, as almost pure oxides, permit us to suppose that at elevated temperatures the solubility of zirconia in alumina could be higher and that ZrO_2 precipitates on primary particles on cooling.

The influence of Al_2O_3 additions on the transformation temperature of ZrO_2 from monoclinic to tetragonal phase ($\alpha \rightarrow \beta$) was also determined. For pure ZrO_2 this temperature was measured as 1162±7°C, but the saturated

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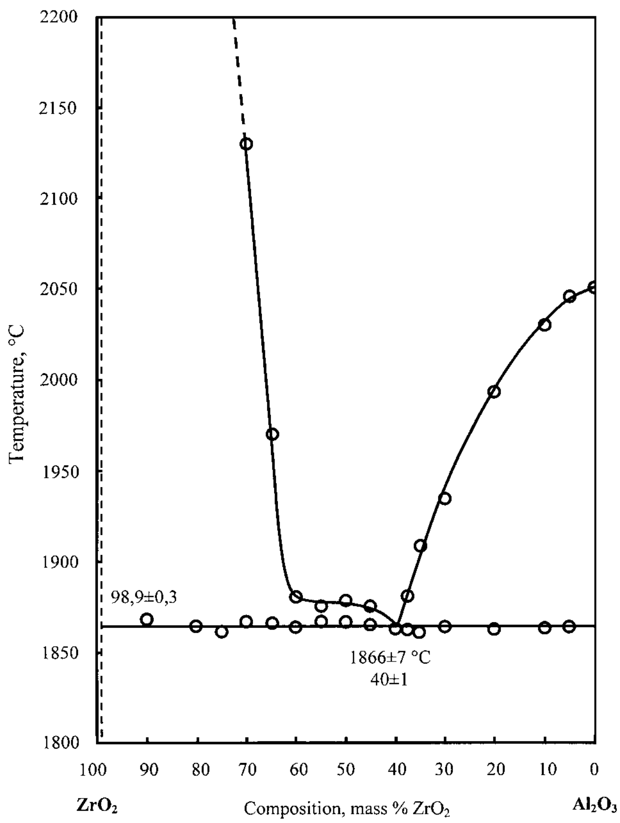

Fig. 1. Phase diagram of the Al_2O_3–ZrO_2 system.

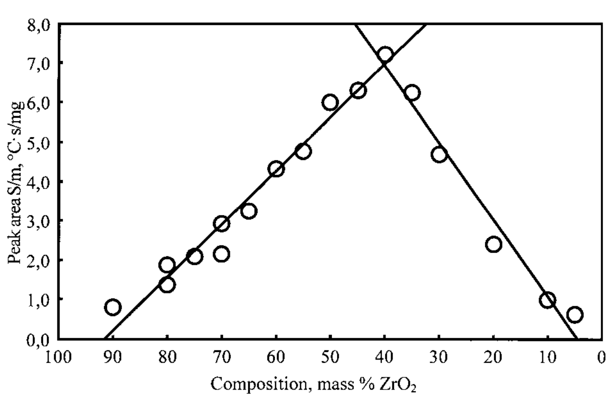

Fig. 2. Normalized eutectic peak area by DTA of the samples of different composition.

SS on ZrO_2 basis (0.7±0.2% mass Al_2O_3) transforms at 1085±5°C. The inverse transitions occur with hysteresis correspondingly at 1055±5 and 995±5°C. These data are close to those reported in [3,7].

In spite of the constancy of phase transition temperature for all samples, the peak areas are not proportional to ZrO_2 content in the sample (Fig. 3); the enthalpy of transformation of pure ZrO_2 from monoclinic to tetragonal phase is 42±5 J/g (5.2±0.6 J/mol) but only 30±5 J/g for a ZrO_2 saturated SS (extrapolated to 99.3% mass ZrO_2). It should be also noted that samples

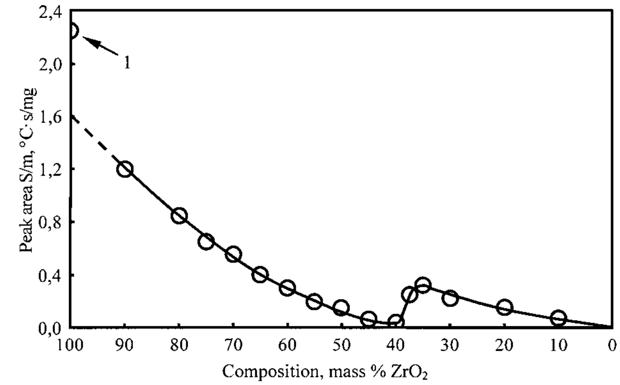

Fig. 3. Normalized $\alpha \rightarrow \beta$ peak area by DTA of the same samples. 1, pure ZrO_2.

Al_2O_3–40% mass ZrO_2 investigated by *x*-ray analysis [9] at room temperature contain up to 99% of tetragonal ZrO_2 which has not transformed into the monoclinic phase. Analogous experiments with slowly cooled samples Al_2O_3–27% mass ZrO_2 [10] demonstrate up to 20% of tetragonal ZrO_2. Both of these observations are in good agreement with our data. A fine eutectic microstructure seems to provide a hard and strong matrix which prevents expansion of ZrO_2 SS particles on cooling. Thereby the eutectic should be more stable to thermal cycling. Visually, the eutectic looks like a milk-white glaze with particle size <0.01 mm while the primary crystals of alumina (transparent cubes) or zirconia (semitransparent dendrites morphologically like squared stars) could be up to 1 mm.

The solubility of Al_2O_3 in ZrO_2 at elevated temperatures could be estimated from the following: the quenched samples have an $\alpha \rightarrow \beta$ transition temperature 120°C below of that of pure ZrO_2 but in annealed samples, this temperature decreases by only 77°C. So it could be estimated that at the eutectic temperature ZrO_2 SS contains 1.1±0.3% mass Al_2O_3. The heat of the $\alpha \rightarrow \beta$ transformation of quenched samples is also 10–20% greater than for annealed samples.

The Mo impurity in any sample, determined by X-ray fluorescence microanalysis, is less than 0.01% mass. Also no weight loss of the samples occurred and no sublimate formed on cold parts of the cell even after 2200°C experiments, so no evaporation of Al_2O_3 (boiling temperature about 3530°C [6]) occurred.

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