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Direct observation of the liquid miscibility gap in the zirconia–silica system

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ABSTRACT

In the technically important ZrO_2–SiO_2 phase system we studied liquid phase formation and solidification by means of the containerless aero acoustic levitation preventing contamination by contact to crucible material. The behaviour of the melt was recorded by a high-speed camera allowing for direct observation of convection, formation and solidification of emulsified reams. For the first time since 1956, we re-treated the liquidus miscibility gap between 59.5 mol-% and 78 mol-% SiO_2 at 2250 °C with the critical point at 2430 °C and 70 mol% SiO_2. Quenching preserved primary microstructures of the monotectic equilibrium with ZrO_2-dendrites in a matrix of silica glass and secondary ZrO_2 but also frozen-in Bénard-Marangoni cell patterns of metastably undercooled of emulsified droplets. These microstructures remind to the partitioning and coagulation behaviour of alkali-borosilicate glasses.

1. Introduction

First studies on the ZrO_2–SiO_2 system aimed at the understanding of phase reactions of zirconia together with other high-melting point materials to make knowledge-based formulations of refractory compositions for the steel and glass production available. In 1920, Washburn & Libman [1] studied melting of various stoichiometries by slowly feeding sintered rods into an acetylene flame and measuring temperature by a pyrometer. They concluded that the melting point of ZrO_2 is in the range of 2700 °C, which still holds today, and that the intermediate phase zircon, $ZrSiO_4$, melts congruently at 2550 °C. Since the extensions of the liquidus curves towards the ZrO_2 and SiO_2 corner, respectively, were not consistent, Washburn & Libman regarded their results as preliminary. In 1931, Barlett [2] continued these studies by fusing sintered rods in an electric arc furnace and quenching the liquid in water, unfortunately without recording temperature. The pellets were subjected to a heat treatment up to 1450 °C in order to establish the stability temperature of zircon ($ZrSiO_4$). During fusion, Barlett observed a liquid phase partitioning yielding zirconia-rich and silica-rich glasses. X-ray pattern proved that the zirconia-rich glass contained monoclinic ZrO_2 and annealing below 1450 °C resulted in the formation of zircon. He, therefore, first time concluded that zircon may thermally decompose into zirconia and silica at higher temperatures.

In 1934, Zhirnova [3] explored the optimum conditions for melting the natural mineral zircon in order to recover the technically important ZrO_2 by dissociation in electric arc furnaces. She published on a SiO_2-rich eutectic at 1705 °C and a ZrO_2-rich at 2220 °C while zircon was considered to melt congruently at 2430 °C. Investigating the peculiarities of thermal expansion and phase transformation of ZrO_2 ceramics with various additives, in 1945-49 Geller & Yavorski and Geller & Lang [4,5] established the first phase diagram with a eutectic reaction between zircon and cristobalite at 1675 ± 5 °C and a peritectic decomposition of zircon into solid ZrO_2 and liquid SiO_2 at 1775 ± 10 °C. Nowadays, we know that the first eutectic is a result of overheating the peritectoidal decomposition of $ZrSiO_4$ into ZrO_2 und cristobalite (cubic SiO_2) at 1673 °C while cristobalite is already eutectically melting together with ZrO_2 at 1687 °C [6].

Uncertainties regarding the fusion of zirconia motivated Toropov & Galakhov [7] in 1956 to re-investigate the liquidus surface of the binary system by starting from pure oxide mixes. Cooling down samples very fast from temperatures >2500 °C obtained by sintering and melting a powder compact inside a tungsten coil yielded dendritic crystallites of a refractive index $n > 2.05$, identified as ZrO_2, grown inside a brown opaque glass. They repeated the experiments with natural zircon crystals and observed "unexpect-

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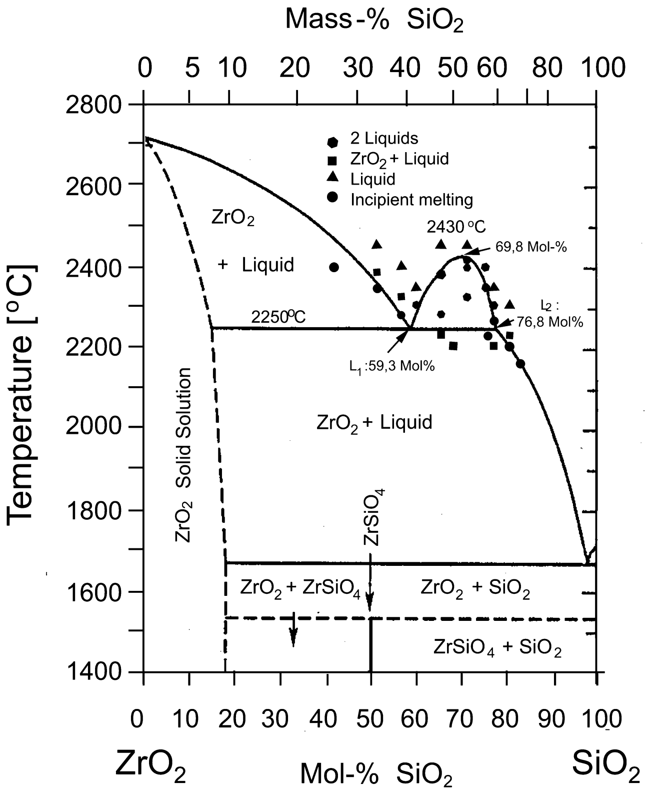

Fig. 1. Phase diagram by Toropov & Galakhov [7]. Solid state part is based on the proposal by Curtis & Sowman [8]. The diagram is re-drawn and transferred to mol-%, the points are original data from the Tables in [7].

edly", as they wrote, two immiscible liquids consisting of emulsified droplets with different concentrations of ZrO_2 precipitates. More careful experiments in the composition range between 25 and 70 mass-% SiO_2 at temperatures between 2200 and 2450 °C established the chemical composition of homogeneous liquid phase formation and the temperature-composition range of the miscibility gap by leaching off the silica with a mix of HF and H_2SO_4 and weighting the recovered unsolvable ZrO_2. In their publication Toropov & Galakhov simply completed the phase diagram by Curtis & Sowman [8] ending at 1800 °C by adding their results as an extension towards higher temperatures. The position of the miscibility gap was given with 59.3–76.8 mol% SiO_2, corresponding to 41–62 mass-% SiO_2 at 2250 °C while the composition of the critical point was 69.8 mol%/53 mass-% SiO_2 at 2430 °C. Fig. 1 presents a re-drawn version of this phase diagram [7] which additionally contains the positions of the originally measured points. It should be pointed out that Toropov & Galakhov also used the unproven solid solubility of SiO_2 in ZrO_2 as proposed by Zhirnova and Curtis & Sowman.

Surprisingly, all phase diagrams and thermodynamic data sets published later make use of these quite early results without any own experimental evidence regarding the liquidus surface, e.g. [9]. Wu [10], for instance, presented a thermodynamic data set obtained by fitted the liquidus line to Toropov's & Galakhov's experimental results which, therefore, resembles the miscibility gap between 58 and 82 mol-% SiO_2 at 2241 °C. For simulation of nuclear core melting and high-temperature reactions with refractory castables Ball et al. [11] presented, among others, a calculated version of the ZrO_2–SiO_2 phase diagram and provided experimental evidence for the immiscibility based on publications by Lang et al. [12], Butterman & Foster [9], Anseau et al. [13], Schuiling et al. [14] and Evans et al. [15] for proof. These sources, however, do not contain any measurements around the miscibility gap but deal with the thermal stability of zircon and its relationship to zirconia while Butterman & Foster [9] made use of the results by Toropov & Galakhov.

In order to gain clarity for the liquidus surface of this technically important system, which is widely needed for the understanding of corrosion phenomena in ZrO_2–SiO_2- and ZrO_2–SiO_2–Al_2O_3-lined glass tanks, we decided to re-investigate the compositions around the miscibility gap by means of aero-acoustic levitation. This technique was chosen as containerless melting is favored for avoiding contamination and reaction by any kind of crucible material. Moreover, liquation and solidification can be recorded by a high-speed camera in real time. To our knowledge, we thus present first time a re-treatment of the liquidus miscibility gap since Toropov & Galakhov and provide direct observation of the formation of ZrO_2- and SiO_2-rich emulsions in the liquid state and of their consolidation, coagulation and further differentiation upon cooling into the metastable state.

2. Materials and methods

2.1. Raw materials and characterisation methods

For the synthesis of compositions in the ZrO_2–SiO_2 system the following raw materials have been used: SiO_2: Amorphous SiO_2: pyrogene silica Aerosil 90, Evonik Industries AG, Hanau, Germany; Crystalline SiO_2: Quartz sand 880, Riedel-DeHaën, Seelze, Germany, purity of both >99.8 mass-% SiO_2; ZrO_2 powder (undoped): Riedel-DeHaën, Seelze, Germany <2 mass-% HfO_2, <0.3 mass-% SiO_2; furthermore: powder from Industriekeramik Hochrhein GmbH, Wutöschingen, Germany, purity > 99.9 mass-% ZrO_2+HfO_2, <0.1 mass-% SiO_2; Zircon powder, $ZrSiO_4$: Alfa Aesar GmbH & Co KG, Karlsruhe, Germany, purity > 99.9 mass-%; furthermore: melt-derived pearls, Mühlmeier Mahltechnik GmbH& Co KG, Bärnau, Germany, >98.0 mass-%, $ZrSiO_4$, which are stoichiometric oxide blends, partially reacted to zircon. Both purity and phase content have been verified by chemical analysis (AAS, ICP) and x-ray diffraction. Powder blends have been produced between 35 and 85 mol-% SiO_2 by intimate mixing the raw materials in an agate mortar.

2.2. Aero acoustic levitation, sample preparation and characterisation

The raw material powder mixes were molten in a copper coquille hearth by a CO_2-laser beam. Pearls of 2–3 mm diameter were obtained and carefully weighted before and after the heat treatment in order to measure the mass loss of SiO_2 due to evaporation.

Levitation was carried out with the aero-acoustic levitator of the Institute of Mineral Engineering at the RWTH Aachen University (Physical Property Measurements Inc., Evanston, Illinois, USA), which is shown in Figs. 2 and 3. A detailed description of the experimental setup was published in [16].

In this setup a spherical sample of about 2–3 mm diameter is levitated on a pre-heated vertical gas flow about 2.5 cm above a Bernoullian nozzle and positioned by means of three pairs of opposed acoustic transducers mounted in an octahedral arrangement. Diode-laser-assisted position sensing of the sample is applied for a feedback control of acoustic forces for counteracting fluctuations in the position of the levitated sample. The sample is heated on opposite sides in the beams of two 240-W-CO_2 lasers (Synrad Inc., Mukilteo, WA, USA). A high-speed camera (V 5.2, Phantom Vision Research Inc., Wayne, NJ, USA) with a long-distance objective lens yields near full-scale images of the levitated sample at up to 2600 frames per second. Sample temperatures are recorded with a pyrometer (Exactus BF 8402, Bayer Catalysts LCC, Rome, Italy) at rates of up to 1000 Hz which is calibrated at the melting point of