Thermal Stability of Zircon (ZrSiO₄) and its Dependence on Natural Impurities in the Raw Materials

The continuing prominence of zircon (ZrSiO₄) as a ceramic and refractory material is due to its excellent thermophysical properties such as low thermal expansion, low thermal conductivity and good corrosion resistance against e.g. glass melts, slags and liquid metal alloys. Accordingly, zircon finds a wide range of application as e.g. a construction material in glass tanks, iron and steel production, energy technology, for molds and cores in precision investment casting or as protective coating of steel-molding tools.

Despite all these established high temperature applications, available information concerning the thermal stability of ZrSiO₄ and the temperature of the solid state dissociation ZrSiO₄ → ZrO₂ + SiO₂ is inconsistent, varying between 1258 °C und 1700 °C, and casts statements concerning service life and long-time behavior into doubt. Thus, the working group has investigated the mechanism of the decomposition reaction of ZrSiO₄, its decomposition temperature and its dependence on type and concentration of impurities in natural zircon raw materials.

Based on heat treatment experiments of numerous natural and synthetic zircon raw materials with known grain sizes and impurity concentrations as well as zircon single crystals the dissociation temperature of ZrSiO₄ could be determined to 1673 ± 10 °C. This solid state dissociation of ZrSiO₄ has been found to be a multiple-stage process, featuring a demixing and gradual enrichment of SiO₂ in form of discrete metastable intermediate compounds like “ZrSi₂O₆” around the simultaneously precipitated ZrO₂ grains (fig. 1). The eutectic temperature in the ZrO₂–SiO₂ system has been determined to 1687 ± 10 °C.

Based on these results the thermodynamic dataset for the ZrO₂–SiO₂ system in the FactSage™ software package, which so far featured a decomposition temperature of 1538 °C, has been optimized with the newly found dissociation temperature of 1673 °C and eutectic temperature of 1687 °C (fig. 2). The combination of this newly created dataset with the databases already available in FactSage™ allows for thermochemical calculations in the system ZrO₂–SiO₂–FeO–Fe₂O₃–TiO₂–Ti₂O₃–MgO (with traces of CaO), which contains the main impurities in natural zircon raw materials like e.g. rutile, ilmenite, magnetite, quartz and corundum.

The thermochemical calculations validate the experimental results which showed that even minor impurities may lead to a decrease of the eutectic temperature in the binary ZrO₂–SiO₂ system, which is merely 14 °C above the dissociation temperature of zircon. Thus, the solid state dissociation of the zircon will be superimposed by the formation of silicate melt at temperatures noticeable below the dissociation temperature. In this melt, a rapid solution of ZrSiO₄ – i.e. primarily its SiO₂ content – and oftentimes dendritic-like precipitation of ZrO₂ is observed (fig. 3).

Fig. 1: Initial state of decomposition of the ZrSiO₄ single crystal, showing a solid state reaction under formation of discrete metastable, intermediate phases at 1660 °C
Additionally, above 1650 °C the dissociation of zircon as a solid state reaction begins which results in a characteristic acceleration of the decomposition kinetics.

Furthermore, thermochemical calculations have helped to verify the influence of specific impurity phases on the decomposition of ZrSiO₄, which have once again been verified by the experimental results. For example, the occurrence of ZrO₂ in samples heat-treated below 1600 °C is often associated with the existence of impurities like corundum (α-Al₂O₃) which in turn reacts with the surrounding zircon grains according to

\[ 2 \text{ZrSiO}_4 + 3 \text{Al}_2\text{O}_3 = \text{Al}_8\text{Si}_2\text{O}_{13} + 2 \text{ZrO}_2 \]

under formation of zirconia and mullite. Thermochemical calculations are also able to explain the absence of characteristic iron and titanium containing impurities (e.g. rutile, ilmenite, magnetite, etc.) in zircon raw materials heat treated above 1500°C. As it turns out, these impurities contribute to a very high degree to the formation of a low melting liquid phase, which can be found in the microstructures as an amorphous solidified glass phase. This phase, in turn, features an enrichment of all impurities like Al₂O₃, Fe₂O₃, TiO₂, CaO, etc. of the zircon raw materials. Thus it has been shown that, besides its dependence on the grain size, the thermal stability of ZrSiO₄ is dominated by the type and concentration of impurities in the zircon raw materials.

In further research the influence of alkaline and alkaline-earth oxides on the decomposition of zircon has been studied by preparing samples of MgO, CaO and Na₂CO₃ and different zircon raw materials according the reactions

- \[ 2 \text{ZrSiO}_4 + \text{Na}_2\text{O} = \text{Na}_2\text{Zr}_2\text{Si}_2\text{O}_{7} + \text{ZrO}_2 \]
- \[ \text{ZrSiO}_4 + 2 \text{CaO} = \text{Ca}_2\text{Zr}_2\text{Si}_2\text{O}_{12} + 3 \text{ZrO}_2 \]
- \[ \text{ZrSiO}_4 + 2 \text{MgO} = \text{Mg}_2\text{SiO}_4 + \text{ZrO}_2 \]

and heat-treating them at temperatures between 900 °C und 1500 °C. The occurring phase reactions and the resulting microstructures have been examined by x-ray diffraction and electron microscopy.

Fig. 2: Calculated optimized phase diagram for the quasi-binary ZrO₂–SiO₂ system

Fig. 3: Thermal decomposition of natural zircon raw material at 1700 °C ([1]: amorphous solidified melt phase with 13.5 wt.% ZrO₂, 81.1 wt.% SiO₂, 5.4 wt.% Al₂O₃; white: ZrO₂; grey: ZrSiO₄)

Literature:

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