IN SITU SYNCHROTRON STUDIES OF OXIDE CERAMICS TO 3,000°C

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A quadrupole halogen lamp furnace (QLF) capable of heating to 2,000°C in air has been developed in our laboratory, in collaboration with Dr. Julius Schneider at the Ludwig Maximillian University in München, Germany. A conical nozzle levitator (CNL) developed by Dr. Richard Weber at Materials Modification in Chicago, Illinois is capable of in situ XRD measurements of oxides to 3,000°C in air. These two instruments were used at the Advanced Photon Sources (APS) at the Argonne National Laboratory, and the QLF was used at the National Synchrotron Light Source II (NSLSII) at Brookhaven National Laboratory to carry out the following experiments:
(i) Thermal expansion measurements in 3-D
(ii) Solid state phase transformations
(iii) Solid state chemical reactions
(iv) In situ determination of phase diagrams

A variety of ceramic and mineral examples are provided to illustrate the seven crystal systems (cubic, tetragonal, orthorhombic, rhombohedral, hexagonal, monoclinic and triclinic). Computer software (Program CTEAS) has been developed to visualize the thermal evolution in 3D for individual {hkl} planes, principle strain directions and whether they are increasing or decreasing. When a crystal undergoes a phase transformation upon heating, the 3D crystal structural, lattice correspondence between the parent and product phases can be identified from the continuity of thermal expansion for planes in the parent phase which approximately “become” planes in the product phase. The example is given of a peritectic reaction in the binary HfO_2-Ta_2O_5 system where $Hf_6Ta_2O_{17}$ decomposes on heating into liquid HfO_2-Ta_2O_5 solid solution plus HfO_2 at 2242 ± 16 °C. A Z = 4, pseudo-subcell is identified which is common to the parent and product phases, which, coupled with vector analysis identifies a lattice correspondence between them, and hence possible orientation relationship.

The oxidation of SiC dispersed into ZrB_2 was studied as an example of a solid state reaction where the kinetics and chemical mechanisms were elucidated. Intermediate crystalline phases that were formed during oxidation of ZrB_2, could be identified and quantified in real time. The oxidation of ZrB_2 phase could be followed independently of concurrent phases, whether amorphous or crystalline, or simultaneous reactions. Increasing the SiC content in the ZrB_2-SiC composites retarded the oxidation of ZrB_2. A novel approach to estimate the thickness of an oxidation layer formed during oxidation of ZrB_2 and ZrB_2-SiC composites, in-situ at high temperatures was proposed, based on fractional conversion of ZrB_2 to ZrO_2

A systematic approach to the rapid production of the high temperature, ternary HfO_2-Ta_2O_5-TiO_2 phase diagrams is presented. This study highlights the combined use of: (i) in-situ high temperature X-ray diffraction on heating to 2,000°C in the QLF, as well as on cooling of liquidi from 3000 ˚C in air in the CNL, and (ii) extraction of common atomic motifs with associated material symmetry analysis. The HfO_2-Ta_2O_5-TiO_2 ternary phase diagram has 4 congruently melting compounds: HfO_2, Ta_2O_5, TiO_2 and $TiTa_2O_7$ and 2 incongruently melting compounds: $Hf_6Ta_2O_{17}$ and $HfTiO_4$. There are no ternary congruently melting compounds. Symmetry relations between $Hf_6Ta_2O_{17}$ and $HfTiO_4$ have been identified. Symmetry decomposition shows that these two structures are simply related to each other via polyhedral rotations. Finally, 10 invariant reactions were identified in this phase space. There is sufficient in-situ high temperature X-ray diffraction data to analyze the ternary between the lowest melting point isotherm and the room temperature isotherm.