

NON-STOICHIOMETRY IN MONOCLINIC ZIRCONIA AND AMORPHOUS ZIRCONIA

Simon C. Middleburgh, Bangor University, U.K.
s.middleburgh@bangor.ac.uk

Michael J.D. Rushton, Bangor University, U.K.

Lee Evitts, Bangor University, U.K.

Iuliia Ipatova, Bangor University, U.K.

William E. Lee, Bangor University, U.K. and Imperial College London, U.K.

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A combination of materials modelling techniques and targeted experimental investigations have identified the manner in which non-stoichiometry is accommodated within both crystalline and amorphous ZrO_2 . Not only is excess oxygen possible in both crystalline and amorphous ZrO_2 , but it is found that there is a high propensity for significant deviations – especially in the amorphous system – forming ZrO_{2+x} . This has clear implications to the behavior and degradation of ZrO_2 as a thermal barrier coating in aerospace and energy components, but also as the boundary oxide protecting zirconium alloys in aggressive environments, including within a water cooled nuclear power reactor.

The behavior was highlighted through a combination of both Raman spectroscopy and associated atomic scale predictions coupled with thermodynamic analysis of the system. As excess oxygen cannot readily oxidize Zr^{4+} ions beyond this charge state, the additional oxygen is accommodated instead as a peroxide ion – O_2^{2-} . This peroxide specie has a distinct covalent bond not expected in the stoichiometric ionic ZrO_2 system that is readily observable using Raman spectroscopy.

Now that excess oxygen accommodation in ZrO_2 has been highlighted, an understanding of how various dopant or alloying elements can impact its behavior can be targeted to improve component reliability. The presence of amorphous phases at grain boundaries is also discussed in terms of potential super-highways for oxygen transport through the oxide system.