Structural evolution during the preparation and heating of nanophase zirconia gels

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

by

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Certificate of authorship and originality

I certify that the work in this thesis has not previously been submitted for a degree, nor has it been submitted as part of requirements for a degree, except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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ANSTO: Australian Nuclear Science and Technology Organisation
ANU: Australian National University
ASRP: Australian Synchrotron Research Program
SRICAT: Synchrotron Research Instrumentation Collaborative Access Team (Advanced Photon Source)
USyd: University of Sydney
UTS: University of Technology, Sydney

Abstract

The chemical preparation of ceramic materials has been widely studied over the past few decades, and provides the potential for excellent control over the microstructure and properties of the final product. This control is dependent on a comprehensive understanding of the microstructure and physical/chemical processes that occur at each stage. Aqueous routes have much potential for adoption by industry, but in many cases a comprehensive understanding of the microstructure and chemistry is lacking, partly due to the complicated aqueous chemistry of many transition-metals.

This investigation has focussed on a specific inorganic, aqueous, sol-gel route for the preparation of pure zirconia (ZrO_2). Zirconia is a ceramic with a wide range of current and potential applications, such as catalysis, fuel-cells, coatings and biomaterials. The emphasis has been placed on the characterisation of the structure at each stage of the route, leading to an understanding of the various mechanisms that are at work. This project has also provided an opportunity to investigate broader issues concerning the solution-based processing of zirconia, particularly those involving the 'metastable' tetragonal phase. This phase is frequently observed to be formed by non-equilibrium methods, but the mechanisms of formation and de-stabilisation are not properly understood.

The studied route consists of a number of stages: the preparation of an aqueous *sol* of 'zirconium hydroxide' particles by forced hydrolysis of a zirconyl nitrate solution; the conversion of the sol to a *gel* by removal of the aqueous phase; the conversion of the gel to a crystalline tetragonal zirconia powder by heating; and transformation of the tetragonal phase to the stable monoclinic phase with further treatment. At each stage of processing a number of aspects of the material structure have been investigated, including the short-range order, crystalline lattice parameters, particle packing, porosity, and speciation of the nitrate anion. This has required a wide range of complementary characterisation techniques, including Raman spectroscopy, XRD, TEM, DTA/TGA, SAXS, dynamic light scattering, EXAFS, NMR, and nitrogen sorption. The importance of techniques that allow changes in structure to be characterised *in-situ* during heating has been emphasised.

The particles in the sol and gel are plate-shaped, approximately 0.5 nm thick and 3 - 4 nm across. They are composed of up to several stacked 'sheets' of zirconium hydroxide, each of which is composed of zirconium atoms arranged in a regular square lattice, joined by double hydroxy-bridges. Detailed evidence for this structure has not been previously reported.

The stages of decomposition of the precursor have been elucidated, including the stages at which oxolation and loss of nitrate occur. The complex crystallisation process at 450°C has been investigated, and a structural mechanism for crystallisation of the 'metastable' tetragonal phase proposed, based on similarities between the tetragonal crystal structure and the disordered sheet structure in the amorphous material just prior to crystallisation. The crystalline material consists of nano-sized crystals, containing unusual intracrystalline mesopores.

The lattice parameters of the tetragonal phase change with increasing heat-treatment, with the unit-cell tetragonality (c/a) increasing from 1.017 to 1.020. This is a previously-unreported phenomenon which may be associated with the stability of the phase. The tetragonal phase transforms to the monoclinic phase after heating to a 'critical temperature' between 900 and 950°C; this temperature is associated with the loss of residual surface nitrate species and/or a substantial increase in the mass diffusion rate. The crystal size and surface area has little influence on the tetragonal-to-monoclinic transformation, a result which is contrary to much previously-published work and that has significant implications for certain theories explaining the stability of the tetragonal phase. The transformation itself occurs during cooling, over a range between 400 and 100°C, and has been studied *in-situ* by time-resolved Raman spectroscopy.

The conclusions of this investigation contribute not only to the understanding of this particular route for processing zirconia, but also to a broader understanding of aqueous zirconium systems, the chemical processing of zirconia, and the tetragonal-to-monoclinic zirconia transformation mechanisms.

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