Time-resolved Studies of Alumina Ceramics Processing with Neutron and Synchrotron Radiation Data

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Abstract

The paper reviews progress for a program of research on alumina ceramics processing, with particular reference to diffraction results achieved using tube x-rays, neutrons and synchrotron radiation. Outcomes from three related studies are examined.

- Calcination of alumina hydrates to α-alumina via intermediate aluminas, including some new results indicating the co-existence of cubic and tetragonal γ-alumina polymorphs following boehmite decomposition.
- Post-sintering heat treatment of debased alumina ceramics to develop/control crystallisation of glassy phase material
- Controlling particle size in zircon/alumina reaction-sintered products using magnesia additions.

Introduction

The Materials Research Group, Curtin University of Technology is conducting a program of research on alumina-matrix ceramic materials for wear-resistant applications. The research aims to make use of alumina powders being produced in Western Australia by the Bayer process. Ceramic processing trials are mainly evaluated by scanning electron microscopy (SEM) and Bragg-Brentano laboratory x-ray diffraction (XRD) after the sintered material has cooled to room-temperature. Neutron diffraction (ND) has proved to be of considerable value for time-resolved studies of selected processing protocols following extensive processing trials which have been evaluated by SEM and XRD. Some use has also been made of room-temperature synchrotron radiation diffraction (SRD) patterns to obtain high resolution diffraction data in selected processing trials. It is envisaged that high-temperature SRD measurements will be conducted in the future to complement the high-temperature ND results in order to characterize the near-surface and bulk character, respectively, of the transformation and sintering mechanisms involved in the processing of alumina-matrix ceramic materials.

The phase transformations occurring in the calcination of the hydrated alumina phase, gibbsite [Al(OH)_3], to α-alumina [Al_2O_3] is of fundamental importance in...
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designing ceramic processing procedures which use partially-calcined starting material. The nature of these transformations has been studied for many years - see review by Wefers and Misra [1]. The pathways involved in the calcination include gibbsite $\rightarrow$ boehmite $[\text{AlOOH}] \rightarrow \gamma$-alumina $[\text{Al}_2\text{O}_3] \rightarrow \theta$-alumina $[\text{Al}_2\text{O}_3] \rightarrow \alpha$-alumina. An aspect of these transitions attracting considerable attention over some 40 years has been the crystal chemistry of the $\gamma$-phase, there having been various reports of both cubic and tetragonal structures. Zhou and Snyder [2] and Li and O'Connor [3] in recent papers described tetragonal models observed using diffraction data recorded at room-temperature after calcined specimens were cooled. The study overviewed here was designed to examine the crystal chemistry of $\gamma$-alumina as the phase forms in the calcination process. The experiment involved using ND analysis of deuterated boehmite to track the temperature dependence of the boehmite $\rightarrow \gamma$-alumina transformation.

The second series of experiments summarised here entailed a study of the development of debased alumina ceramics for wear-resistant applications using locally-sourced minerals. The feedstock materials were selected to facilitate development of liquid-phase-sintering protocols for alumina-matrix ceramics. In view of the wear-resistance focus, grain growth control during the ceramic firing was of critical importance. The experiments described here focussed on the possibility of using post-sintering crystallisation to change the microstructure of the ceramic by crystallising phases from the glassy (amorphous) component. The ‘cocktail’ under investigation was a mixture of $\alpha$-alumina, kaolinite, talc, calcite and wollastonite. Prospective phases for the microstructure included $\alpha$-alumina, spinel $[\text{MgO.} \text{Al}_2\text{O}_3]$, mullite $[3\text{Al}_2\text{O}_3.2\text{SiO}_2]$ and anorthite $[\text{CaO}.\text{Al}_2\text{O}_3.\text{SiO}_2]$. The heat treatment research concentrated on the possibility of reduced the level of glassy phase material in favour of ‘abrasive’ crystalline phases in order to increase wear resistance.

The third study was an investigation of the efficacy of using reaction sintering of $\alpha$-alumina and zircon $[\text{ZrSiO}_4]$, plus sintering agents, to produce alumina-matrix ceramics for wear-resistant applications. The results described briefly here are for a processing trials with 1 % by weight MgO added as a sintering aid. The prospective phases for the trial included $\alpha$-alumina, tetragonal and monoclinic zirconia $[\text{ZrO}_2]$, spinel and mullite. The particular interest was to determine whether particular phases are present at low concentrations, eg spinel and mullite.

The results of the experiments are described more fully in recent PhD theses [4-6] by three of the authors. Journal papers from the theses have been published or are in preparation - see references 7 and 8.

**Experimental**

Time-resolved ND measurements were performed with the MRPD neutron powder diffractometer at the HIFAR reactor operated by ANSTO at Lucas Heights, near Sydney, Australia. Supporting SRD data were collected with the BIGDIFF Debye-Scherrer diffractometer at the Australian National Beamline Facility, Photon Factory, Tsukuba, Japan.

High-temperature ND data were recorded with the ANSTO MRPD instrument described in reference 9. It is configured with 24 He$^3$ detectors. For these studies, measurements were made at a wavelength of 1.664 Å; with a detector range of $2\theta = 0$-
138° and 2θ step size = 0.1°; and counting time of 40-50 seconds per step, as determined by a monitor which corrected for neutron flux variations. The specimens were heated with vertical alumina tube furnaces - the boehmite transformation study being performed to a limiting temperature of 1100°C and the debased alumina ceramics study with a 1600°C furnace.

Use of the BIGDIFF SRD instrument for characterizing ceramic materials is explained in references 10 and 11. For SRD data acquisition in these studies, a Si (111) channel-cut monochromator was used to provide a wavelength close to that for the CuKα doublet (1.5378 Å). A slit combination placed in front of the monochromator controlled the length and width of the capillary exposed to SR. The incident beam dimensions were set at (i) a height of 0.8 mm to completely immerse the specimen in the SR beam and (ii) a width of 1.0 cm. SRD data were measured with specimens packed in low-absorption lithium borate glass capillaries (0.5 mm diameter, 0.01 mm wall thickness). Specimen were rotated during data collection and the exposure time was 15 minutes. The data were measured with the BIGDIFF instrument volume held at a pressure below 1 torr which largely eliminated air scatter attenuation at the wavelength employed.

Laboratory XRD data were measured at Curtin University with flat-plate specimens using a Siemens D500 Bragg-Brentano diffractometer configured as follows - Cu tube operating at 40 kV and 30 mA (weighted mean wavelength = 1.5418 Å), incident beam divergence 1°, receiving slit 0.15”, post-diffraction graphite monochromator, NaI detector with pulse discrimination, 2θ step size 0.04°, counting time 1 s/step, 2θ range = 5-150° and pattern acquisition time ≈ 60 minutes.

Results and Discussion

**Boehmite to Gamma-Alumina Transformation**

Figure 1 shows the phase transformations occurring as a deuterated boehmite specimen was heated. Between room temperature and 300°C, the ND pattern features are entirely due to boehmite, with Rietveld phase composition analysis of the data showing clear indications that the phase is becoming increasingly disordered as the temperature approaches 300°C. No indications of gibbsite were found in the room temperature data as the deuteration process, involving exchange with D2O water, had resulted in complete transformation of gibbsite to boehmite.

Clear indications of γ-alumina are found between 400 and 1000 °C, with θ-alumina first appearing at 750°C and then α-alumina at 900°C. The most prominent γ-alumina feature is the doublet in the 400°C pattern at 2θ ≈ 50°. This peak is of particular interest as the doublet form of the peak is clearly indicative of tetragonal character.

Rietveld phase composition analysis of all data sets gave unexpected results in relation to the crystal chemistry of γ-alumina. Figure 2 shows particularly interesting results. Difference plots from the Rietveld modelling with the 400°C data in Figure 2 show how the feature at 2θ ≈ 50° gives excellent agreement between the observed and calculated ND patterns when co-existence of the cubic and tetragonal γ-alumina phases is assumed. The measured data cannot be adequately modelled using only the cubic phase or the tetragonal phase. Plots of phase composition versus temperature in reference 4 clearly show that both phases co-exist between 400-1000 °C. At 400°C,
the level of the tetragonal phase exceeds that of the cubic phase. The relative concentration of the cubic $\gamma$-alumina phase then increases at the expense of the tetragonal phase, becoming dominant by 750°C. Thus tetragonal $\gamma$-alumina is favoured when boehmite transforms, but then the formation of the cubic phase becomes more likely as the calcination temperature rises.

Further details of these interesting results are available in reference 4, and will be published in the journal literature. At the time of writing further experiments are being planned in relation to this finding.

Figure 1. MRPD ND diffraction patterns for decomposition of boehmite from room temperature (RT) to 1100°C. Wavelength = 1.664Å. Each diffraction pattern (except RT) has been shifted vertically using successive offsets of 500 counts.
Figure 2. Rietveld difference plots for the 400°C MRPD data set in Figure 1.
Top: difference plot assuming that the γ-alumina is entirely tetragonal.
Below: difference plot assuming co-existence of the cubic and tetragonal γ-alumina phases.

Debased Alumina Ceramic Processing

Figure 3 shows the results of an SRD evaluation of a heat treatment trial in which the liquid-phase-sintered specimen has been re-heated to 1150°C and then held at that temperature for 24 h to promote crystallisation of the intergranular glassy phase without changing the grain size. The heat-treated specimen was then slowly cooled to room temperature at 1°C per minute. The data clearly show the value of using SRD rather than XRD to define the low-concentration phases. The heat-treated specimen
contains considerably more spinel, and anorthite has crystallised from the intergranular glassy material.

Figure 3. Comparison of SRD and XRD data for heat treatment of debased alumina ceramic. Top: SRD patterns (wavelength = 1.5378 Å) for 'as-fired' ceramic sintered at 1400°C and after post-sintering heat treatment at 1150°C - see text. Below: corresponding XRD data for CuKα radiation. Peak labels: A = α-alumina, S = spinel, An = anorthite and C = ‘contaminant’ feature. The numbers associated with the peak symbols are JCPDS intensities.
Dynamic ND data showing the crystallisation of spinel and anorthite from the intergranular glass during post-sintering cooling are presented in Figure 4. These results are consistent with the SRD data described above. The ND results, while lacking the sensitivity and pattern resolution evident in the SRD data, have the advantage of providing characterisation of the bulk material 'at-temperature'.

Figure 4. MRPD ND data for debased alumina ceramics during post-sintering cooling to room temperature. Top: slow-cooled from 1400°C to room temperature at 3°C per minute. Below: rapid-cooled to room-temperature at 30°C per minute. See Figure 3 for symbols.
Reaction-Sintering of Zircon with Excess Alumina

Reference 11 gives a detailed description of the experiment outlined in the Introduction. The SRD and XRD results presented here in Figure 5 illustrate further the value of SRD data to define low-concentration phases. The superior dynamic range of the SRD data for phase definition gave an important result for the material in terms of mechanical properties as the level of mullite in the ceramic was determined to be considerably less than 1% by weight.

Figure 5. SRD and XRD patterns for alumina-matrix produced by reaction sintering of excess alumina and zircon. Top: part of SRD pattern (wavelength = 1.5378 Å). Below: part of XRD pattern (CuKα radiation). Symbols: A = α-alumina, S = spinel, T = tetragonal zirconia and M = monoclinic zirconia. The numbers associated with the peak symbols are JCPDS intensities.

Conclusion

The paper has illustrated the value of using both ND and SRD to study ceramic sintering processes in real time as these complementary techniques provide bulk and near-surface information respectively. The authors intend to make routine use of real-time ND and SRD in studying such systems.
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References