

In situ diffraction study of self-recovery in vacuum decomposed Al_2TiO_5

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Available Online at: www.austceram.com/ACS-Journal

Abstract

The ability of decomposed Al_2TiO_5 to undergo self-recovery or reformation during vacuum annealing was characterised by in-situ neutron diffraction. It is shown that the process of phase decomposition in Al_2TiO_5 was reversible and that reformation occurred readily when decomposed Al_2TiO_5 was re-heated above 1300°C . The kinetics of isothermal and temperature-dependent self-recovery was modelled using the Avrami equation. The influence of grain-size on the Avrami kinetics of self-recovery was also evident.

Keywords: Neutron diffraction, Al_2TiO_5 , decomposition, self recovery, vacuum-annealing

Introduction

Aluminium titanate (Al_2TiO_5) is an excellent refractory and thermal shock resistant material due to its relatively low thermal expansion coefficient and high melting point. It is one of several materials which is isomorphous with the mineral pseudobrookite (Fe_2TiO_5) [1,2]. In this structure, each Al^{3+} or Ti^{4+} cation is surrounded by six oxygen ions forming distorted oxygen octahedra. These AlO_6 or TiO_6 octahedra form (001) oriented double chains weakly bonded by shared edges. This structural feature is responsible for the strong thermal expansion anisotropy which generates localised internal stresses to cause severe microcracking. Although this microcracking weakens the material, it imparts a desirable low thermal expansion coefficient and an excellent thermal shock resistance.

However, at elevated temperature, Al_2TiO_5 is only thermodynamically stable above 1280°C and undergoes a eutectoid-like decomposition to $\alpha\text{-Al}_2\text{O}_3$ and TiO_2 (rutile) within the temperature range $900\text{--}1280^\circ\text{C}$ [3-13]. This undesirable decomposition has limited its wider application. In our recent studies [12-15], microstructure and furnace atmosphere have been observed to have a profound influence on the thermal stability of Al_2TiO_5 . For instance, the decomposition rate of Al_2TiO_5 at 1100°C was significantly enhanced in vacuum (10^{-4} torr) or argon where $>90\%$ of Al_2TiO_5 decomposed after only 4 h

annealing when compared to less than 10% in atmospheric air [12,13]. This suggests that the process of decomposition of Al_2TiO_5 is susceptible to environmental attack or sensitive to the variations in the oxygen partial pressure during ageing. The stark contrast in the mechanism of phase decomposition is believed to arise from the vast differences in the oxygen partial pressure that exists between air and vacuum. A similar phenomenon has been observed for Al_2TiO_5 samples having different grain sizes whereby the rate of phase decomposition increased as the grain size decreased [14]. The reason for this grain-size effect is unclear at this stage although the kinetics of decomposition may be rate limited by processes occurring at the grain boundaries. It has also been shown that the process of decomposition in Al_2TiO_5 is reversible whereby self-recovery occurs readily when decomposed Al_2TiO_5 is re-heated above 1300°C [15, 16].

In this paper, we present results on the role of grain size on the capability of previously decomposed Al_2TiO_5 to self-recover in vacuum when it is reheated above 1300°C . The temperature-dependent thermal stability and the capacity of Al_2TiO_5 to self-recover have been characterized using high-temperature neutron diffraction to study the phase changes in real time.

Experimental Methods

Sample Preparation

The starting powders used for the synthesis of Al_2TiO_5 (AT) consisted of high purity commercial alumina (99.9% Al_2O_3) and rutile (99.5% TiO_2). One mole of alumina powder and one mole of rutile powder were initially mixed using a mortar and pestle. The powder mixture was then wet mixed in ethanol using a Turbula mixer for 2.0 h. The slurry was then dried in a ventilated oven at 100°C for 24 h. The dried powder was uniaxially-pressed in a steel die at 150 MPa to form cylindrical bars of length 20 mm and diameter 15 mm, followed by sintering in a air-ventilated furnace at (a) 1400°C in air for 1 h to achieve a fine-grained microstructure ($\sim 1\text{-}3\mu\text{m}$), and (b) 1600°C in air for 4 h to achieve coarse-grained ($\sim 20\text{-}30\mu\text{m}$) Al_2TiO_5 . The samples were then completely decomposed by annealing them in an air-ventilated furnace at 1100°C for 10 h. Figure 1 shows the typical diffraction patterns of samples before and after decomposition.

In-Situ Neutron Diffraction (ND)

In-situ neutron diffraction was used to monitor the structural evolution of self-recovery in previously decomposed Al_2TiO_5 at high-temperature in real time. Diffraction patterns were collected using the Polaris – the high intensity, medium resolution powder diffractometer at the UK pulsed spallation neutron source ISIS, Rutherford Appleton Laboratory. Sample was held in a basket made from thin tantalum wire and mounted in a Risø-design high-temperature furnace (Risø National Laboratory, Roskilde). Fitted with a thin tantalum foil element and tantalum and vanadium heat shields, this furnace is capable of reaching 2000°C and operates under a high dynamic (i.e. continuously pumped) vacuum (pressure $< 7.5 \times 10^{-6}$ torr).

Temperature monitoring and control was achieved using type W5 thermocouples connected to Eurotherm 3504 controllers. Collimating slits (manufactured from neutron-absorbing boron nitride) mounted on the furnace in the scattered beam direction enable diffraction patterns free from Bragg reflections off the tantalum element and heat shields to be collected in the Polaris $2\theta = 90^\circ$ detectors.

A reference diffraction pattern was collected at room temperature while the furnace was initially evacuated, then Al_2TiO_5 samples were heated rapidly up from room temperature to 1450°C for the coarse-grained sample and 1500°C for the fine grained sample. Figure 2 shows the heating protocols used during the experiment for each sample. The relative abundance of phases present was computed using the Rietveld

method. The models used to calculate the phase abundance were Maslen *et al.*¹⁷ for alumina, Epicier *et al.*¹⁸ for Al_2TiO_5 , and Howard *et al.*¹⁹ for rutile. The software used to analyze the data was Fullprof-WinPlotR.

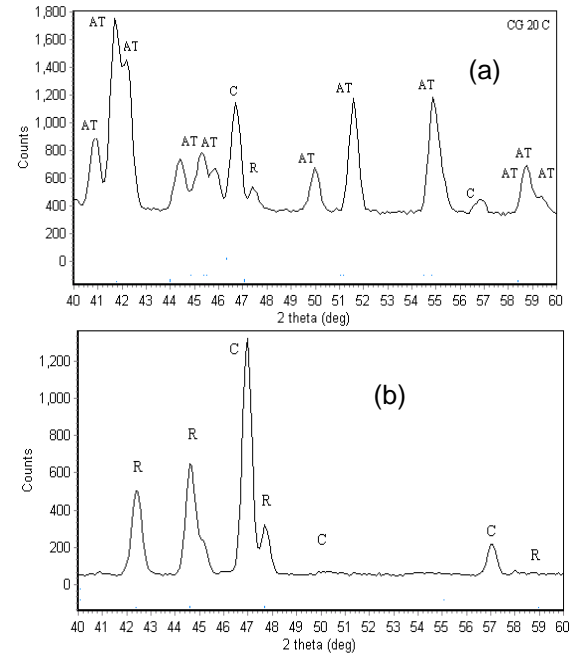


Figure 1: Typical neutron diffraction plots of Al_2TiO_5 (a) before and (b) after decomposition at 1100°C in air. [Legend: AT = Al_2TiO_5 ; C = corundum; R = rutile]

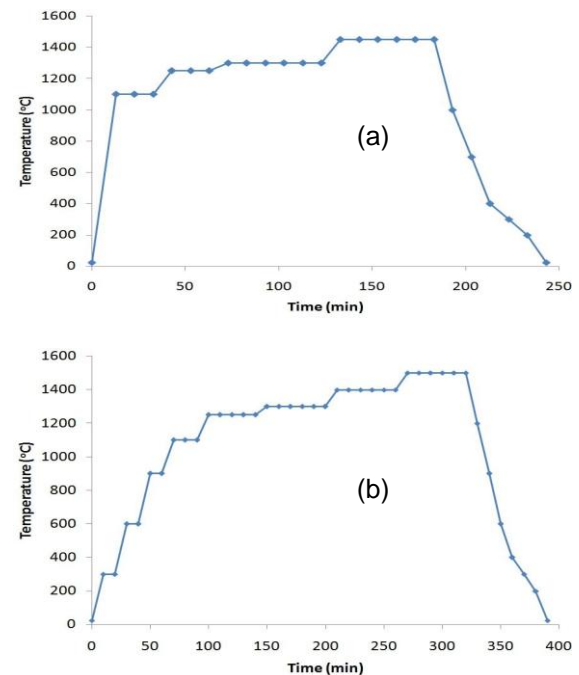
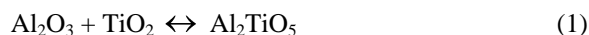


Figure 2. The heating protocols used the in-situ neutron diffraction experiment for (a) coarse-grained and (b) fine-grained sample.

RESULTS AND DISCUSSION

Effect of grain size on Self-Recovery

Figure 3 shows the capability of coarse-grained decomposed Al_2TiO_5 to self-recover when it was reheated from room temperature to 1450°C . It is clearly shown that self-recovery takes place at $\sim 1450^\circ\text{C}$ through the rapid reaction of corundum and rutile to form Al_2TiO_5 but with <40 wt% phase purity. In contrast, >65 wt% Al_2TiO_5 reformed for the fine-grained sample and the process of self-recovery commenced at a lower temperature of $\sim 1400^\circ\text{C}$ (Fig. 4). It appears that fine grains impart a greater rate of atomic diffusion along the grain boundaries to promote the reformation of Al_2TiO_5 from reaction between Al_2O_3 and TiO_2 as follows:



To the best of our knowledge, this is the first time that grain size has been shown to affect the propensity of self-recovery in Al_2TiO_5 . This capability of self-recovery further suggests the process of self-reformation is diffusion-controlled and reversible as indicated in Equation (1). However, it should be noted here that the ability of decomposed Al_2TiO_5 to self-recover in vacuum is much inferior when compared to near-complete self-recovering when annealed in air.^{15,16} The underlying reason for this difference is unclear although the role of oxygen partial pressure in the furnace may play a vital role. Nonetheless, the implication of this phenomenon is far-reaching whereby it may be possible to restore the decomposed Al_2TiO_5 to its original condition by thermal annealing in air at $>1400^\circ\text{C}$.

Avrami Kinetics of Self-Recovery

The role of grain size on the kinetics of self-recovery during vacuum-annealing of decomposed Al_2TiO_5 at elevated temperature was modelled using the Avrami equation (see Fig. 5). The Avrami rate constant (k) and Avrami exponent (n) were respectively determined to be $8.15 \times 10^{-15} \text{ min}^{-n}$ and 5.88 for coarse-grained and $5.62 \times 10^{-7} \text{ min}^{-n}$ and 2.50 for fine-grained.

The isothermal self-recovery of coarse-grained Al_2TiO_5 during vacuum-annealing at 1450°C was fitted with both the least-squares linear regression and the modified Avrami equation (see Fig. 6) The corresponding least-squares regression exponent (R^2) and Avrami constants (k and n) of isothermal decomposition were determined to be 0.96, $6.23 \times 10^{-5} \text{ min}^{-n}$ and 2.02 respectively. This suggests that the kinetics of Al_2TiO_5 self-recovery is better described by an exponential Avrami rate reaction than a linear rate reaction.

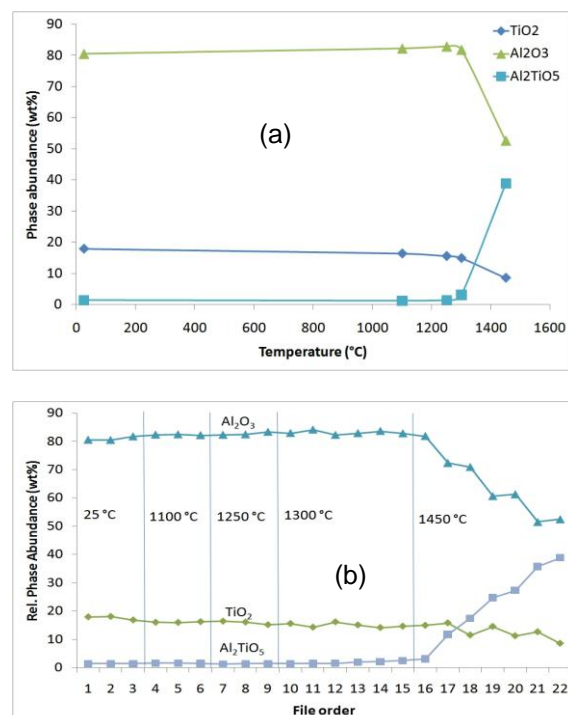


Fig. 3: The propensity of coarse-grained al_2tio_5 to self-recover during reheating to 1450°C in vacuum as a function of: (a) temperature, and (b) time & temperature.

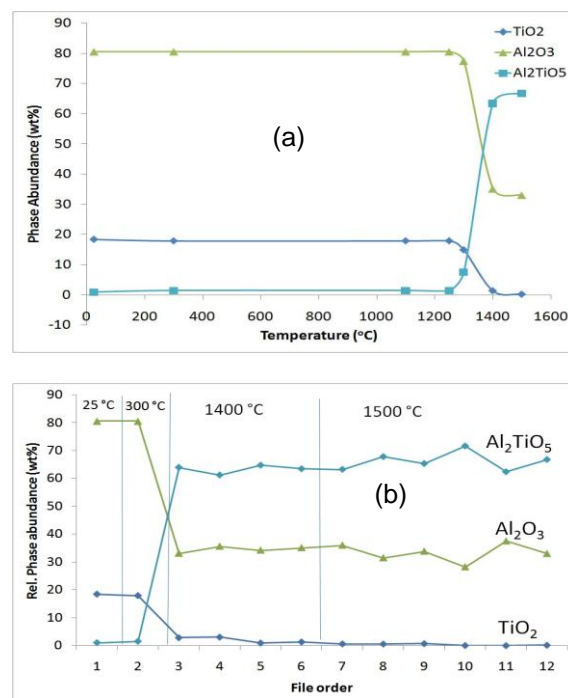


Fig. 4: The propensity of fine-grained al_2tio_5 to self-recover during reheating to 1500°C in vacuum as a function of: (a) temperature, and (b) time & temperature.

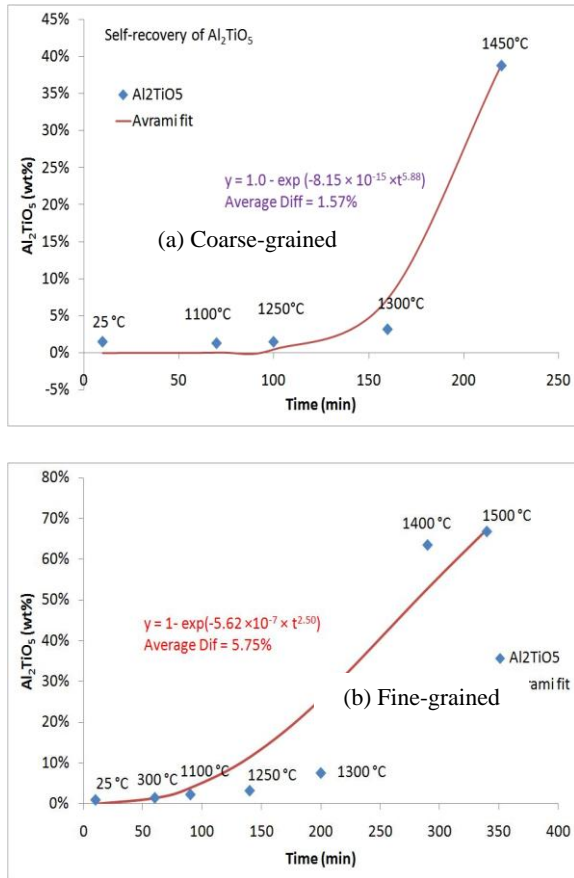


Fig. 5: Effect of (a) coarse-grain and (b) fine-grain on the Avrami fit of self-recovery in vacuum-annealed Al_2TiO_5 at elevated temperature.

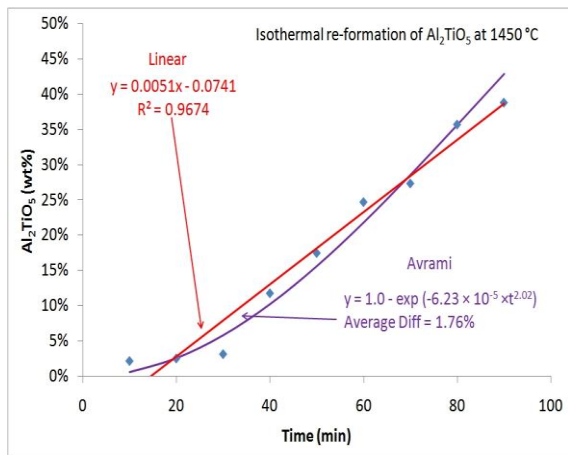


Fig. 6: Least-squares linear regression and Avrami fits of self-recovery during isothermal vacuum-annealing of coarse-grained Al_2TiO_5 at 1450 °C.

Microstructural Features

Fig. 7 (a) shows the typical microstructures of as-decomposed fine-grained Al_2TiO_5 prior to vacuum-annealing. The existence of corundum (grey grains) and rutile (white grains) in the microstructure is

evident. Following vacuum-annealing at 1500 °C for 0.5 h, self-recovery occurred with the formation of Al_2TiO_5 grains. A similar process of self-recovery also occurred for the coarse-grained sample vacuum-annealed at 1450 °C for 0.5 h (Fig. 7c). As the microstructure becomes coarser, the degree of self-recovery appears to become less and is least for the coarse-grained sample. This observation is consistent with the neutron diffraction results shown in Figs. 3 & 4 above.

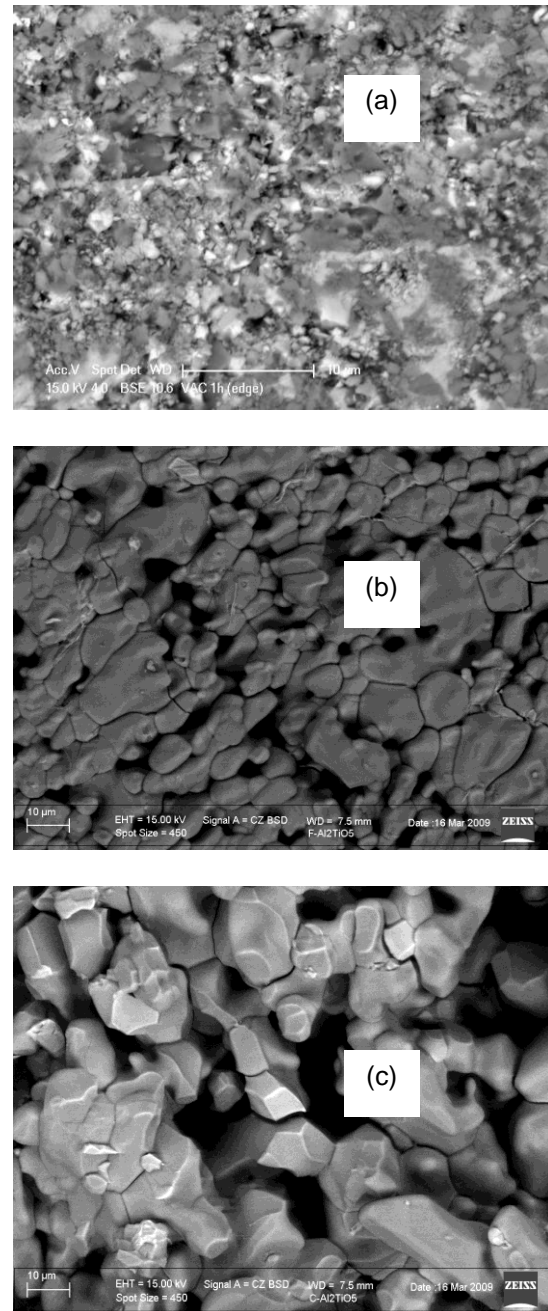


Fig. 7: Scanning electron micrographs showing the microstructures of (a) decomposed fine-grained Al_2TiO_5 , (b) self-recovered fine-grained Al_2TiO_5 , and (c) self-recovered coarse-grained Al_2TiO_5 .

Conclusions

The effect of grain size on the capacity of Al_2TiO_5 to undergo self-recovery in the temperature range 20-1500°C was dynamically examined by neutron diffraction. The ability of Al_2TiO_5 to self-recover in vacuum increased as the grain size decreased probably through an enhanced atomic diffusion process by virtue of increased surface area and grain boundaries. The Avrami kinetics of Al_2TiO_5 self-recovery was also dependent on grain size.

Acknowledgement

This work was supported by a LIEF grant (LE0882725) and the collection of neutron diffraction data was conducted at ISIS (RB1010064) which was provided by the Science and Technology Facilities Council, with financial support from an AMRFP grant. We thank Dr. R. Smith of ISIS and Prof. E. Wu of IMR for assistance with the data collection.

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