In situ diffraction study of self-recovery in vacuum decomposed \( \text{Al}_2\text{TiO}_5 \)

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Abstract
The ability of decomposed \( \text{Al}_2\text{TiO}_5 \) 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 \( \text{Al}_2\text{TiO}_5 \) was reversible and that reformation occurred readily when decomposed \( \text{Al}_2\text{TiO}_5 \) 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, \( \text{Al}_2\text{TiO}_5 \), decomposition, self recovery, vacuum-annealing

Introduction
Aluminium titanate (\( \text{Al}_2\text{TiO}_5 \)) 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 (\( \text{Fe}_2\text{TiO}_5 \)) [1,2]. In this structure, each \( \text{Al}^{3+} \) or \( \text{Ti}^{4+} \) cation is surrounded by six oxygen ions forming distorted oxygen octahedra. These \( \text{AlO}_6 \) or \( \text{TiO}_6 \) 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, \( \text{Al}_2\text{TiO}_5 \) is only thermodynamically stable above 1280°C and undergoes a eutectoid-like decomposition to \( \alpha \)-\( \text{Al}_2\text{O}_3 \) and \( \text{TiO}_2 \) (rutile) within the temperature range 900-1280°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 \( \text{Al}_2\text{TiO}_5 \). For instance, the decomposition rate of \( \text{Al}_2\text{TiO}_5 \) at 1100°C was significantly enhanced in vacuum (10⁻¹⁴ torr) or argon where >90% of \( \text{Al}_2\text{TiO}_5 \) 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 \( \text{Al}_2\text{TiO}_5 \) 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 \( \text{Al}_2\text{TiO}_5 \) 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 \( \text{Al}_2\text{TiO}_5 \) is reversible whereby self-recovery occurs readily when decomposed \( \text{Al}_2\text{TiO}_5 \) 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 \( \text{Al}_2\text{TiO}_5 \) to self-recover in vacuum when it is reheated above 1300°C. The temperature-dependent thermal stability and the capacity of \( \text{Al}_2\text{TiO}_5 \) 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$_2$TiO$_5$ (AT) consisted of high purity commercial alumina (99.9% Al$_2$O$_3$) 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 an air-ventilated furnace at (a) 1400°C in air for 1 h to achieve a fine-grained microstructure (~1-3μm), and (b) 1600°C in air for 4 h to achieve coarse-grained (~20-30μm) Al$_2$TiO$_5$. 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$_2$TiO$_5$ 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 < 7.5×10$^{-6}$ 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 2θ =90° detectors.

A reference diffraction pattern was collected at room temperature while the furnace was initially evacuated, then Al$_2$TiO$_5$ 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$_2$TiO$_5$, and Howard et al.$^{19}$ for rutile. The software used to analyze the data was Fullprof-WinPlotR.

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Figure 1: Typical neutron diffraction plots of Al$_2$TiO$_5$ (a) before and (b) after decomposition at 1100°C in air. [Legend: AT = Al$_2$TiO$_5$; C = corundum; R = rutile]

Figure 2. The heating protocols used the in-siti 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 $\text{Al}_2\text{TiO}_5$ to self-recover when it was reheated from room temperature to 1450°C. It is clearly shown that self-recovery takes place at ~1450°C through the rapid reaction of corundum and rutile to form $\text{Al}_2\text{TiO}_5$ but with <40 wt% phase purity. In contrast, >65 wt% $\text{Al}_2\text{TiO}_5$ reformed for the fine-grained sample and the process of self-recovery commenced at a lower temperature of ~1400°C (Fig. 4). It appears that fine grains impart a greater rate of atomic diffusion along the grain boundaries to promote the reformation of $\text{Al}_2\text{TiO}_5$ from reaction between $\text{Al}_2\text{O}_3$ and $\text{TiO}_2$ as follows:

$$\text{Al}_2\text{O}_3 + \text{TiO}_2 \leftrightarrow \text{Al}_2\text{TiO}_5$$ (1)

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 $\text{Al}_2\text{TiO}_5$. 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 $\text{Al}_2\text{TiO}_5$ 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 $\text{Al}_2\text{TiO}_5$ to its original condition by thermal annealing in air at >1400°C.

Avrami Kinetics of Self-Recovery

The role of grain size on the kinetics of self-recovery during vacuum-annalining of decomposed $\text{Al}_2\text{TiO}_5$ 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 $8.15 \times 10^{-15}$ min\(^n\) and 5.88 for coarse-grained and $5.62 \times 10^{-7}$ min\(^n\) and 2.50 for fine-grained.

The isothermal self-recovery of coarse-grained $\text{Al}_2\text{TiO}_5$ during vacuum-annalining 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 $\times 10^{-5}$ min\(^n\) and 2.02 respectively. This suggests that the kinetics of $\text{Al}_2\text{TiO}_5$ self-recovery is better described by an exponential Avrami rate reaction than a linear rate reaction.

Fig. 3: The propensity of coarse-grained $\text{Al}_2\text{TiO}_5$ 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 $\text{Al}_2\text{TiO}_5$ 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 Al₂TiO₅ at elevated temperature.

Fig. 6: Least-squares linear regression and Avrami fits of self-recovery during isothermal vacuum-annealing of coarse-grained Al₂TiO₅ at 1450 °C.

Microstructural Features
Fig. 7 (a) shows the typical microstructures of as-decomposed fine-grained Al₂TiO₅ 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 Al₂TiO₅ 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 Al₂TiO₅, (b) self-recovered fine-grained Al₂TiO₅, and (c) self-recovered coarse-grained Al₂TiO₅.
Conclusions

The effect of grain size on the capacity of Al₃TiO₅ to undergo self-recovery in the temperature range 20-1500°C was dynamically examined by neutron diffraction. The ability of Al₃TiO₅ 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 Al₃TiO₅ self-recovery was also dependent on grain size.

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References