DYNAMIC NEUTRON DIFFRACTION STUDY OF THERMAL STABILITY AND SELF-RECOVERY IN ALUMINIUM TITANATE

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ABSTRACT

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. However, Al_2TiO_5 unstable and undergoes a eutectoid-like decomposition to α-Al_2O_3 and TiO_2 (rutile) at the temperature range of 900-1280°C. In this paper, we describe the use of high-temperature neutron diffraction to study (a) the phenomenon of self-recovery in decomposed Al_2TiO_5, and (b) the role of grain size on the rate of isothermal decomposition at 1100°C. It is 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, and the rate of phase decomposition increases as the grain size decreases.

INTRODUCTION

Aluminium titanate (Al_2TiO_5) is an excellent refractory and thermal shock resistant material due to its relatively low thermal expansion coefficient (~1×10^{-6} °C^{-1}) and high melting point (1860°C). 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.

At elevated temperature, Al_2TiO_5 is only thermodynamically stable above 1280°C and undergoes a eutectoid-like decomposition to α-Al_2O_3 and TiO_2 (rutile) within the temperature range 900-1280°C.[3-11] This undesirable decomposition has limited its wider application. Hitherto, the role of grain size on the rate of phase decomposition is poorly understood but experimental evidences suggest a nucleation and growth controlled process. It is generally agreed that the decomposition rate peaks at 1100°C and that residual alumina particles might act as preferred nucleation sites for the decomposition.[3]

In recent studies by Low and co-workers,[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 is significantly enhanced in vacuum (10^{-4} torr) or argon where >90% of Al_2TiO_5 decomposed after only 4 h soaking when compared to less than 10% in atmospheric air.[12-14] 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, although less profound, has been observed for Al_2TiO_5 with a distinct difference in grain size. However, it is unclear whether there is a critical grain size associated with this phenomenon. The reason for this grain-size effect is unclear at this stage although it may be closely related to its greater tendency for microcracking as the grain size increases. The microcracking

phenomenon is closely related to the material microstructure and thermal expansion anisotropy.[16-18] Below a critical grain size, the elastic energy of the system is insufficient to nucleate microcracks during cooling and thus causing no degradation to the mechanical strength. The density of microcracks increases drastically with grain size once the critical value is exceeded.

In this paper, we present results on the role of grain size on the isothermal stability of Al_2TiO_5 at 1100°C as well as its capability to self-recover when it is reheated following decomposition. The temperature-dependent thermal stability and isothermal decomposition of Al_2TiO_5 have been dynamically monitored and characterized using neutron diffraction to study the structural changes occurring during phase decomposition 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 (FG) microstructure (~1-3μm); (b) 1500°C in air for 2 h to achieve a medium-grained (MG) microstructure (~5-10μm), and (c) 1600°C in air for 4 h to achieve coarse-grained (CG) (~30-50μm) Al_2TiO_5.

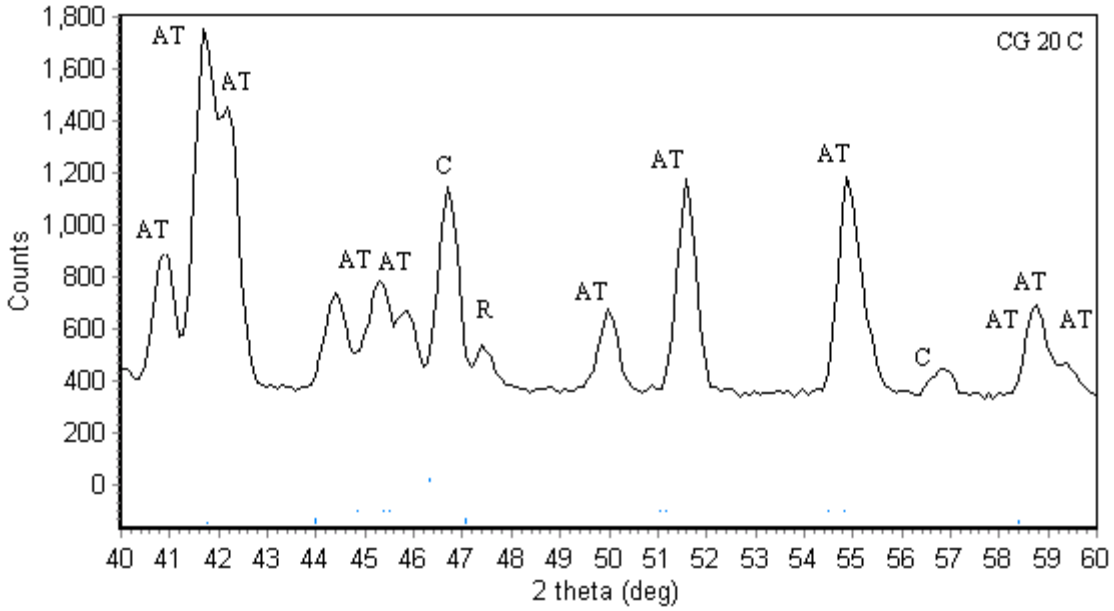
Neutron Diffraction (ND)

A medium resolution powder diffractometer (MRPD) located at the Australian Nuclear Science and Technology Organization (ANSTO) in Lucas Heights, NSW was used for neutron diffraction study of the thermal stability of Al_2TiO_5. The effect of grain size on the isothermal stability of Al_2TiO_5 was dynamically monitored at 1100°C in air atmosphere for up to 10 hours. A decomposed medium-grained Al_2TiO_5 sample was used for the study of self-recovery by reheating it from room temeperature to 1450°C. In addition, the temperature range and the onset of thermal decomposition of Al_2TiO_5 in the temperature range 20 – 1400°C was investigated. The operation conditions of the MRPD were λ = 1.667 Å, 2θ range = 4-138°, step size = 0.1°, counting time ~40-50 s/step, monochromator of 8 Ge crystals (115 reflection), and 32 ^{3}He detectors 4° apart. The relative abundance of phases present was computed using the Rietveld method. The models used to calculate the phase abundance for MRPD were Maslen *et al.*[19] for alumina, Epicier *et al.*[20] for Al_2TiO_5, and Howard *et al.*[21] for rutile. The software used to analyze the data was Rietica 1.7.7.

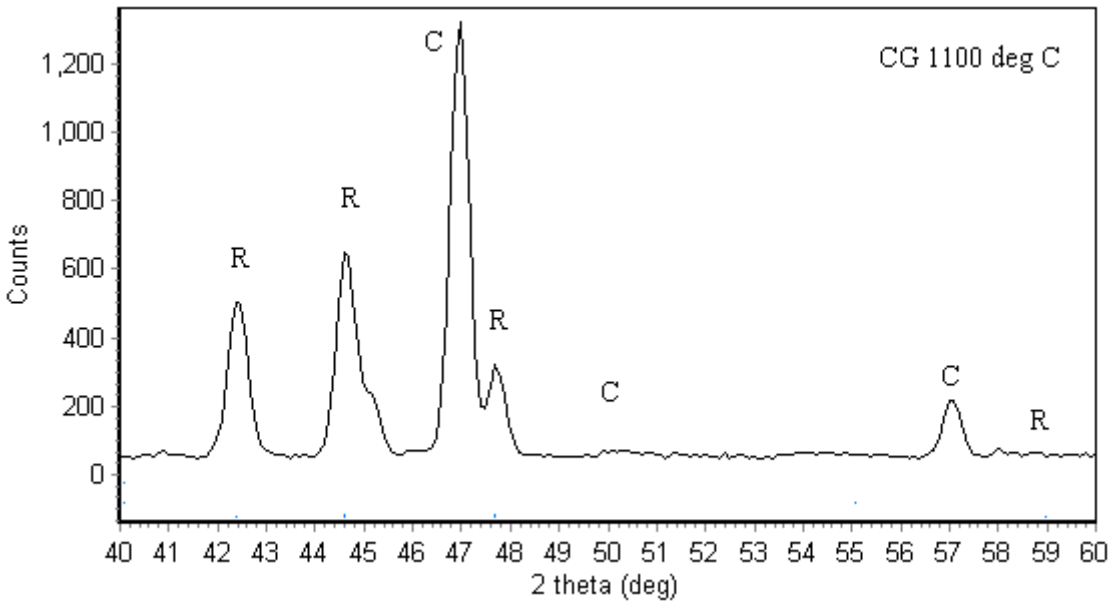
RESULTS AND DISCUSSION

Effect of Grain Size on Phase Stability

Figure 1 shows the typical neutron diffraction plots of Al_2TiO_5 with CG and MG microstructures before and after thermal decomposition at 1100°C for 10 h to form corundum and rutile. The corresponding diffraction plots for the FG sample are shown in Fig. 2. The good quality of Rietveld refinement plots for three samples are shown in Fig. 3 where “goodness-of-fits” of between 2.5 -3.5 were achieved. The Bragg factors (R_B) obtained for corundum, Al_2TiO_5 and rutile were between 2-5 – 2.7, 3.0 – 3.2, and 1.9 – 2.1 respectively.

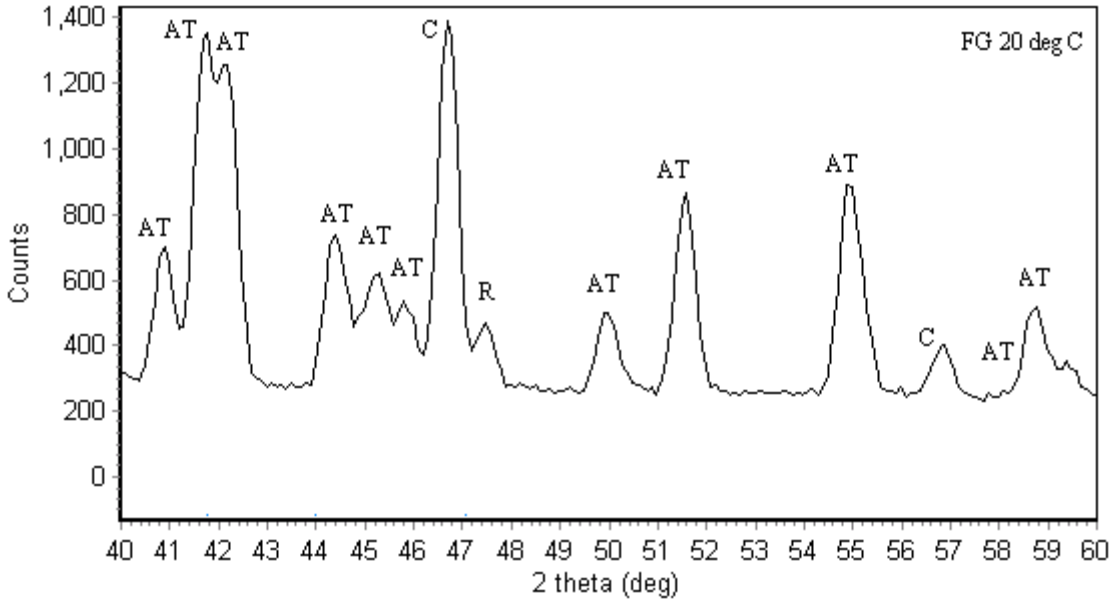


(a)

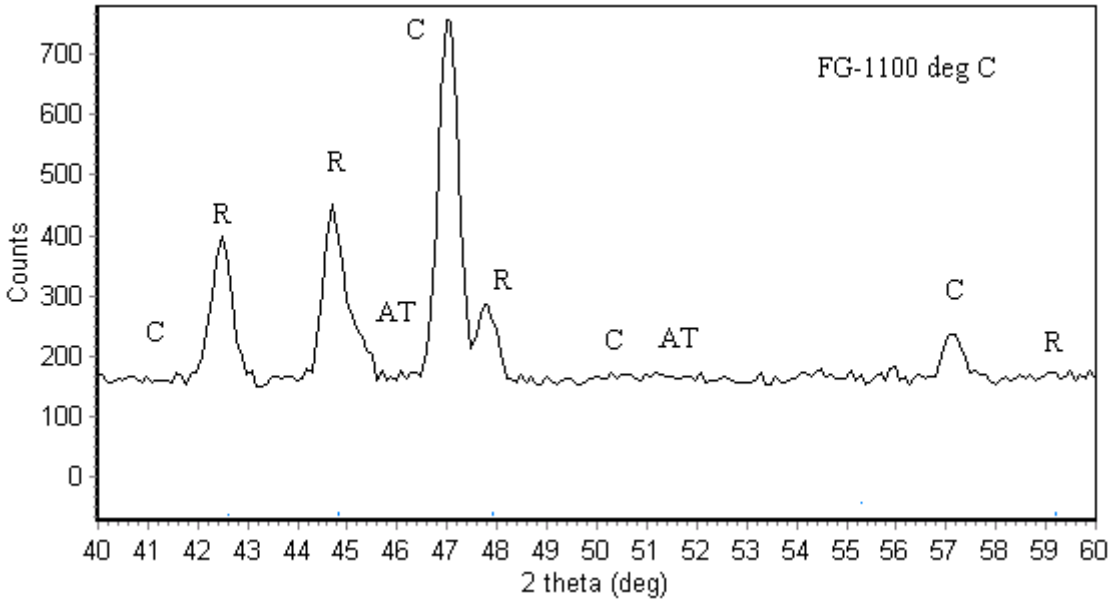


(b)

Fig. 1: Typical neutron diffraction plots of as-sintered CG or MG Al_2TiO_5 (a) before and (b) after isothermal decomposition at 1100°C for 10 h. [Legend: AT = Al_2TiO_5; C = corundum; R = rutile]



(a)



(b)

Fig. 2: Typical neutron diffraction plots of as-sintered FG Al_2TiO_5 (a) before and (b) after isothermal decomposition at 1100°C for 10 h. [Legend: AT = Al_2TiO_5; C = corundum; R = rutile]

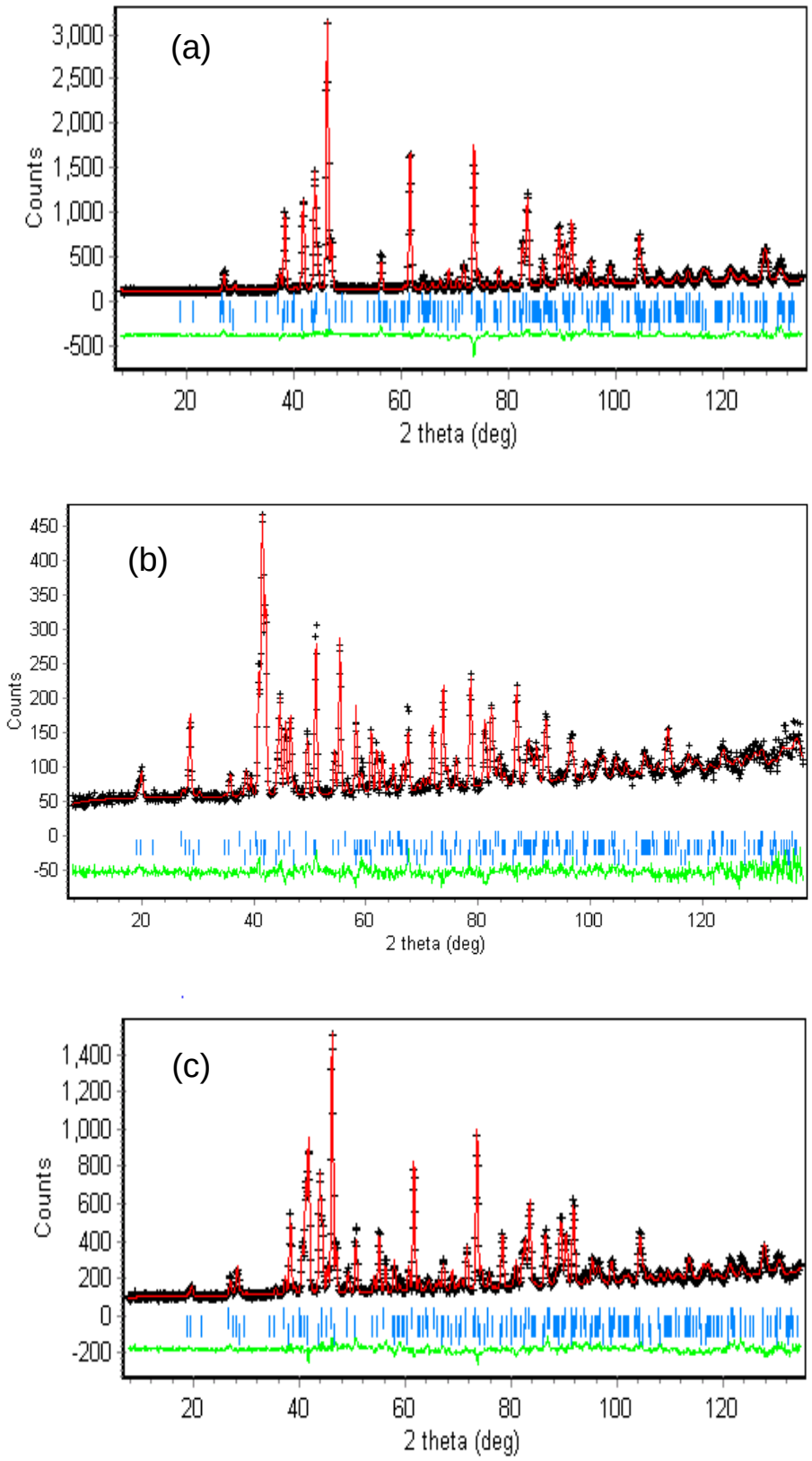


Fig. 3: Rietveld refinement plots of Al_2TiO_5 after isothermal decomposition at 1100°C: (a) FG, (b) MG, and (c) CG.

The profound effect of grain size on the isothermal stability of in air at 1100°C is revealed in Fig. 4. Clearly, coarse-grained Al_2TiO_5 exhibits a slowest rate of thermal decomposition when compared to its medium-grained and fine-grained counterparts. To the best of our knowledge, this is the first time that grain size has been shown to affect the propensity of thermal degradation in Al_2TiO_5. However, it is unclear whether there is a critical grain size associated with this phenomenon. The reason for this grain-size effect is unclear at this stage although it may be closely related to its greater tendency for stress-relief through microcracking as the grain size increases. The microcracking phenomenon is closely related to the material microstructure and thermal expansion anisotropy.[13-15] Below a critical grain size, the elastic energy of the system is insufficient to nucleate microcracks during cooling and thus causing no degradation to the mechanical strength. The density of microcracks increases drastically with concomitant stress-relief once the grain size exceeds a critical value. It is hypothesized that the release of residual stresses helps to reduce phase decomposition.

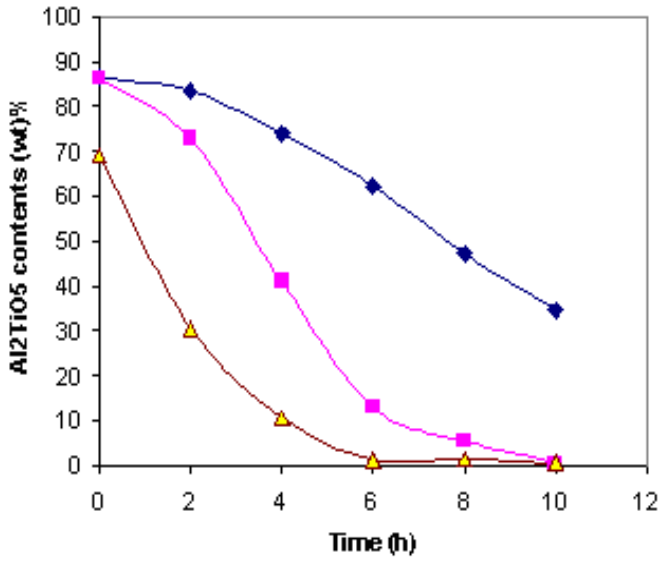


Fig. 4: Effect of Al_2TiO_5 grain size on the propensity of isothermal decomposition at 1100°C in air. [Legend: CG (♦); MG (■); FG (▲)]

Fig. 5 (a) shows the typical microstructure of as-sintered coarse-grained AT prior to isothermal ageing where the presence of fine microcracks within certain grains is clearly evident. The formation of these microcracks can be attributed to the pronounced thermal expansion anisotropy of AT during cooling from an elevated temperature. The formation of these stress-relief microcracks is believed to impart a low fracture strength but high thermal shock resistance to AT and improved thermal stability. Following isothermal-ageing in air at 1000°C for 10 h, both needle-like and angular particles could be seen to form on the surface of Al_2TiO_5 grains (Fig. 5b). Based on the energy dispersive spectrocopy (EDS) results,[15] these nano-sized particles were identified as surface by-products (ie. Al_2O_3 and TiO_2) of thermally decomposed AT. This may indicate that the initial nucleation process of thermal decomposition of AT is surface-initiated and the growth kinetics are diffusion-controlled or temperature and time dependent.

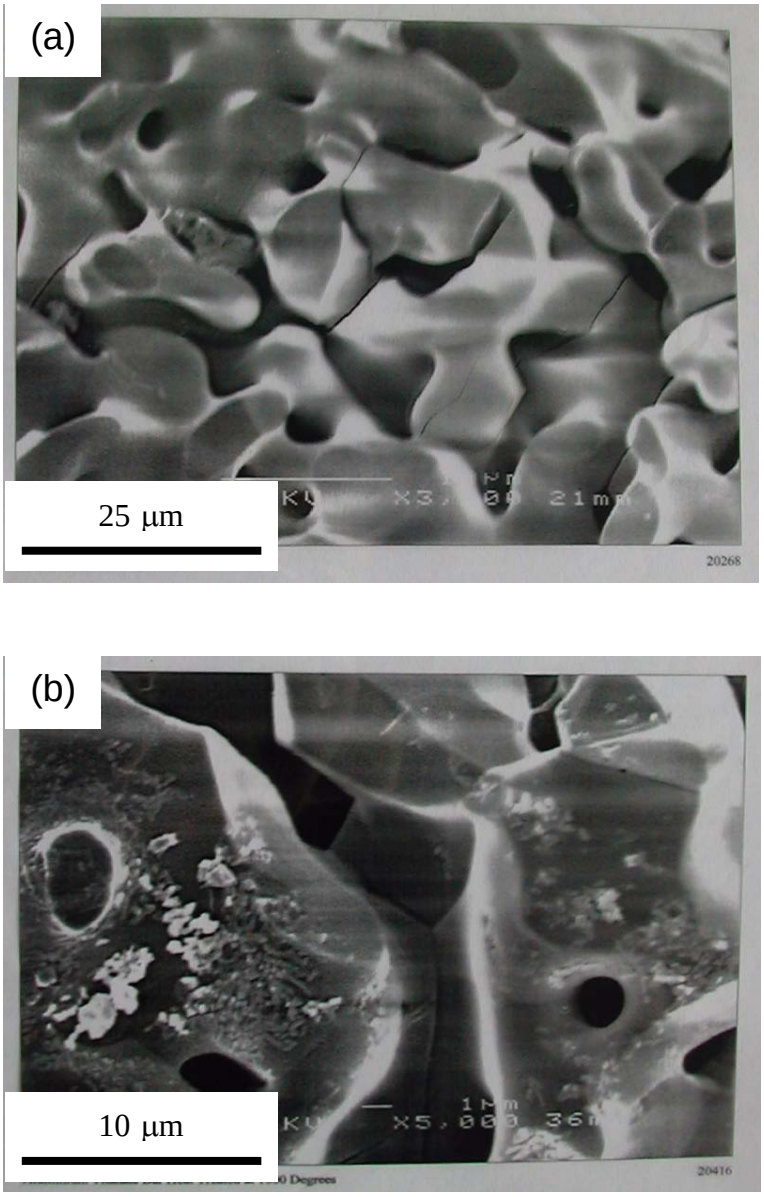


Fig. 5: Scanning electron micrographs of coarse-grained AT (a) before decomposition and (b) after isothermal decomposition at 1100°C. Note the presence of microcracks within certain grains in (a).

The stark contrast in the microstructures of decomposed Al_2TiO_5 with different grain sizes is shown in Figure 6. The light regions in the microstructures indicate the locations of rutile grains following phase decomposition of Al_2TiO_5. A large amount of rutile can be seen in the fine-grained sample which indicates extensive phase decomposition (Fig. 6a). As the microstructure becomes coarser, the degree of phase decomposition appears to become less and is least in the coarse-grained sample (Fig. 6a). This observation is consistent with the neutron diffraction results shown in Fig. 3 above. However, the implication of this work may be a deterrent to materials scientists to develop high-strength nano-structured Al_2TiO_5 which might be highly susceptible to phase decomposition, unless it is stabilized by additives such as MgO, Fe_2O_3 and SiO_2.

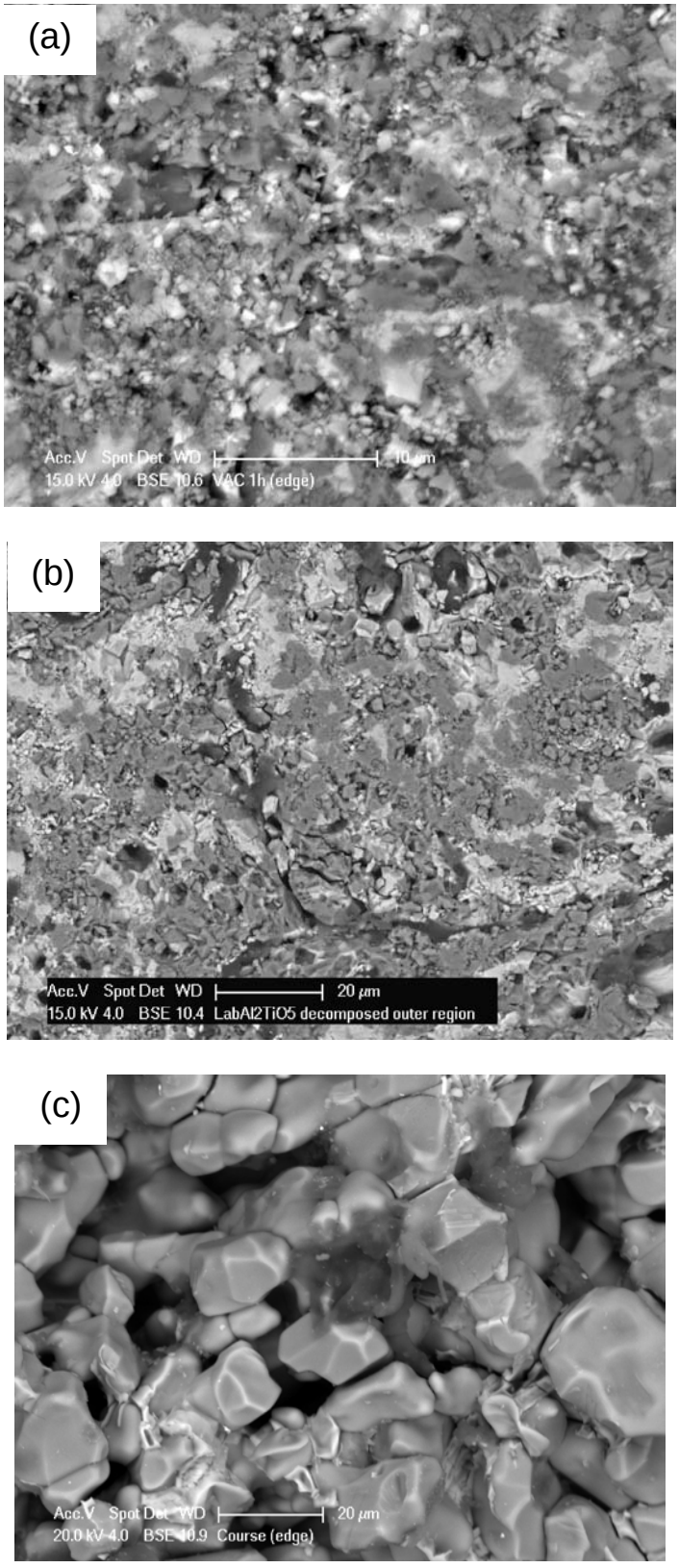


Fig. 6: Scanning electron micrographs showing the microstructures of decomposed Al_2TiO_5 with different grain sizes: (a) FG, (b) MG, and (c) CG. Note the increasing degree of phase decomposition as the grain size decreases from (c) to (a).

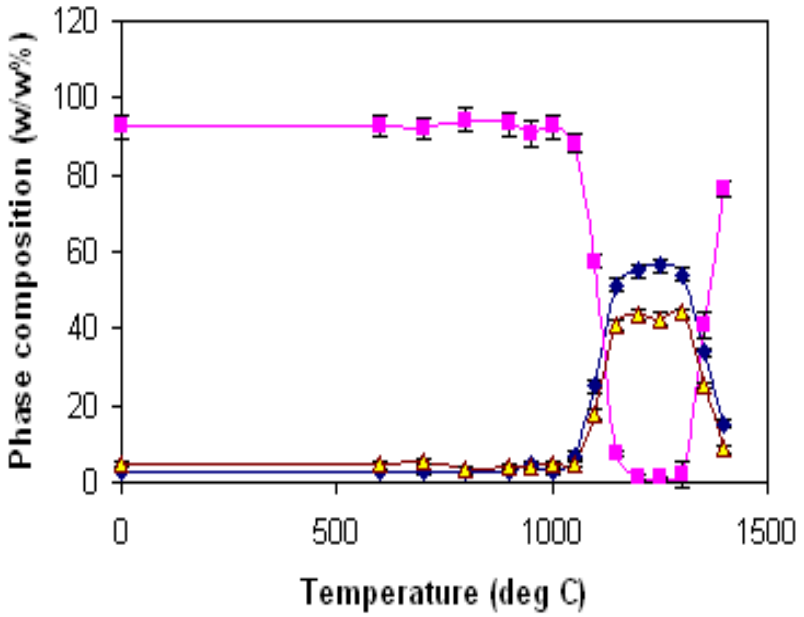


Fig. 7: Thermal stability of Al_2TiO_5 over 20–1400°C as revealed by high-temperature neutron diffraction. Note the display of pronounced thermal decomposition at ~1100 - 1300°C. Errors bars indicate two estimated standard deviations ±2σ. [Legend: ■ = Al_2TiO_5; ♦ = Al_2O_3; Δ = TiO_2]

Phenomenon of Self-Recovery

The thermal stability of Al_2TiO_5 in the temperature range 20 – 1400°C as revealed by neutron diffraction is shown in Fig. 7. Clearly, Al_2TiO_5 is stable up to ~1100°C and becomes unstable at between ~1150 - 1300°C. Beyond 1300°C, the thermal decomposition is arrested and the phase stability is restored. This implies that the process of thermal decomposition is reversible or recoverable provided the restricted temperature range of between ~1100 - 1300°C is not transgressed. This process of self-recovery or reversible reaction can be described as follows:

$$Al_2O_3 + TiO_2 \leftrightarrow Al_2TiO_5 \quad (1)$$

Figure 8 provides further evidence of self-recovery in decomposed Al_2TiO_5 when it was reheated from room temperature to 1450°C for 2 h. It is clearly shown that self-recovery takes place through the rapid reaction of corundum and rutile to form Al_2TiO_5 with >98 wt% phase purity. This capability of self-recovery further suggests the process of decomposition is spontaneous and reversible as indicated in Equation (1). 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 at >1400°C.

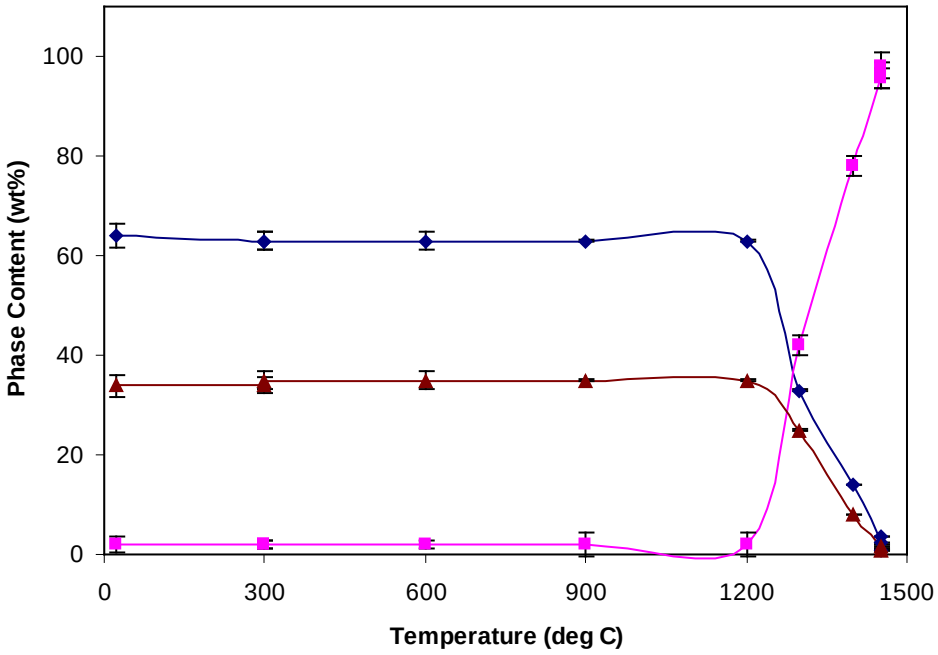


Fig. 8: Reformation of Al_2TiO_5 through self-recovery in decomposed Al_2TiO_5. [Legend: ■ = Al_2TiO_5; ♦ = corundum; ▲ = rutile]

CONCLUSIONS

The effect of grain size on the thermal stability of Al_2TiO_5 at 1100°C and the phenomenon of self-recovery in the temperature range 20-1400°C have been dynamically examined by neutron diffraction. The thermal stability of Al_2TiO_5 increases as the grain size increases probably through the formation of stress-relief microcracks. The process of phase decomposition is reversible and self-recovery occurs readily when decomposed Al_2TiO_5 is re-heated above 1300°C.

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REFERENCES

[1]A.E. Austin and C.M. Schwartz, The Crystal Structure of Aluminium Titanate, *Acta Cryst*. **6**, 812-13 (1953).

[2]B. Morosin and R.W. Lynch, Structure Studies on Al_2TiO_5 at Room Temperature and at 600°C, *Acta Cryst*. B. **28**, 1040-1046 (1972).

[3]H.A.J. Thomas and R. Stevens, Aluminium Ttitanate – a Literature Review. Part 1: Microcracking Phenomena, *Br. Ceram Trans. J*. **88**, 144-90 (1989).

[4]H.A.J. Thomas and R. Stevens, Aluminium Titanate - A literature Review. Part 2: Engineering Properties and Thermal Stability, *Br. Ceram Trans. J*. **88**, 184-190 (1989).

[5]V. Buscaglia, P. Nanni, G. Battilana, G. Aliprandi, and C. Carry, Reaction Sintering of Aluminium Titanate: 1 - Effect of MgO Addition, *J. Eur. Ceram. Soc*. **13**, 411-417 (1994)

[6]G. Tilloca, Thermal Stabilization of Aluminium Titanate and Properties of Aluminium Titanate Solid Solutions, *J. Mater. Sci*. **26**, 2809-2814 (1991).

[7]E., Kato, K. Daimon and Y. Kobayashi, Factors Affecting Decomposition Temperature of β- Al_2TiO_5, *J. Am. Ceram. Soc*. **63**, 355-356 (1980).

[8]R.W. Grimes and J. Pilling, Defect Formation in β-Al_2TiO_5 and its Influence on Structure Stability, *J. Mater. Sci*. **29**, 2245-49 (1994).

[9]M. Ishitsuka, T. Sato, T. Endo and M. Shimada, Synthesis and Thermal Stability of Aluminium Titanate Solid Solutions, *J. Am. Ceram. Soc.* **70**, 69-71 (1987).

[10]B. Freudenberg and A. Mocellin, Aluminum Titanate Formation by Solid-State Reaction of Coarse Al_2O_3 and TiO_2 Powders, *J. Am. Ceram. Soc*. **71**, 22-28 (1988).

[11]B. Freudenberg and A. Mocellin, Aluminium Titanate Formation by Solid State Reaction of Al_2O_3 and TiO_2 Single Crystals, *J. Mater. Sci*. **25**, 3701-3708 (1990).

[12]I.M. Low, D. Lawrence, and R.I. Smith, Factors Controlling the Thermal Stability of Aluminium Titanate in Vacuum, *J. Am. Ceram. Soc*. **88**, 2957-2961 (2005).

[13]I.M. Low, Z. Oo and B. O'Connor, Effect of Atmospheres on the Thermal Stability of Aluminium Titanate, *Physica B: Condensed Matter*, **385-386**, 502-504, (2006).

[14]I.M. Low and Z. Oo, Reformation of Phase Composition in Decomposed Aluminium Titanate, *Mater. Chem. & Phys.* **111**, 9-12 (2008).

[15]A. Jones and I.M. Low, Microstructural Characteristics of Isothermally-Aged Aluminium Titanate Ceramics, pp.185-186 in *Proc. of AUSTCERAM 2002* (Eds. I.M. Low & D.N. Phillips), 30 Sept – 4 Oct. 2002, Perth, WA.

[16]Y. Ohya, Z. Nakagawa and K. Hamano, Crack Healing and Bending Strength of Aluminium Titanate Ceramics at High Temperature, *J. Am. Ceram. Soc*. **71**, C23-C33 (1988).

[17]Y. Ohya and Z. Nakagawa, Grain Boundary Microcracking Due to Thermal Expansion of Al_2TiO_5 Ceramics at High Temperature, *J. Am. Ceram. Soc*. **70**, C184-C186 (1987).

[18]K. Hamano, Y. Ohya and Z. Nakagawa, pp. 129-137 in *Int. Journal of High Tech. Ceram*. Elsevier Science Publishers Ltd., UK. (1985)

[19]E.N. Maslen, V.A. Streltsov, N.R. Streltsova, N. Ishizawa and Y. Satow, Synchrotron X-Ray Study of the Electron Density in α-Al_2O_3, *Acta Crystallographica*, **B49**, 937-980 (1993).

[20]T. Epicier, G. Thomas, H. Wohlfromm and J.S. Moya, High Resolution Electron Microscopy Study of the Cationic Disorder in Al_2TiO_5, *J. Mater. Res*. **6**, 138-145 (1991).

[21]C.J. Howard, T.M. Sabine and F. Dickson, Structural and Thermal Parameters for Rutile and Anatase, *Acta Cryst. B*, **47**, 462-468 (1991).