EFFECT OF GRAIN SIZE AND CONTROLLED ATMOSPHERES ON THE THERMAL STABILITY OF 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 is only thermodynamically stable above 1280°C and undergoes a eutectoid-like decomposition to α-Al_2O_3 and TiO_2 (rutile) at the temperature range of 900-1280°C. Hitherto, the effect of grain size and atmosphere on the kinetics of decomposition is poorly understood but experimental evidences suggest a nucleation and growth controlled process. In this paper, we describe the role of grain size and controlled atmospheres on the thermal stability of Al_2TiO_5. In particular, the effects of grain size and oxygen partial pressure on the rate of isothermal decomposition of Al_2TiO_5 at 1100°C have been investigated. Results show that the thermal stability of Al_2TiO_5 increases as the grain size and oxygen partial pressure increases. However, both the on-set temperature nor the temperature range of Al_2TiO_5 thermal decomposition are not affected by the variation of oxygen partial pressure present in the furnace atmosphere.

KEYWORDS: Thermal stability, Al_2TiO_5, grain size, atmosphere, neutron diffraction, decomposition.

INTRODUCTION

Aluminium titanate (Al_2TiO_5) is an excellent refractory and thermal shock resistant material due to its relatively low thermal expansion coefficient ($\sim 1 \times 10^{-6}$ °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.

In addition, 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 [3-7]. This undesirable decomposition has limited its wider application. Hitherto, the mechanisms of decomposition are 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]. The impact of this thermal instability can be improved through the use of various stabilisers such as MgO, Fe_2O_3 and SiO_2.

In recent studies by Low and co-workers [8-12], both grain size and the oxygen partial pressure of the furnace atmosphere has 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 [8,12]. 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.. In addition, it is still unclear whether the variation of oxygen partial pressure has any influence on the range and on-set of decomposition temperature of Al_2TiO_5.

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 [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 grain size once the critical value is exceeded.

In this paper, we present results on the effect of grain size and controlled atmospheres on the isothermal stability of Al_2TiO_5 at 1100°C as well as its decomposition behaviour in the temperature range 20-1400°C. 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 microstructure ($\sim$1-3μm); (b) 1500°C in air for 2 h to achieve a medium-grained microstructure ($\sim$5-10μm), and (c) 1600°C in air for 4 h to achieve coarse-grained ($\sim$30-50μm) Al_2TiO_5.

Neutron diffraction (ND)

A medium resolution powder diffractometer (MRPD) located at the Australian Nuclear Science and Technology Organisation (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 12. Medium-grained Al_2TiO_5 samples were used for the study of isothermal stability in different atmospheres, namely air, argon (99.99% purity) and 50% argon - 50% oxygen. In addition, the influence of atmosphere on 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*. [16] for alumina, Epicier *et al*. [17] for Al_2TiO_5, and Howard *et al*. [18] for rutile. The software used to analyse the data was Rietica 1.7.7.

RESULTS AND DISCUSSION

Effect of Grain Size

Figure 1 shows the effect of grain size on the isothermal stability of in air at 1100°C. 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 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 grain size once the critical value is exceeded.

Fig. 2(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 presence of these microcracks is believed to impart a low fracture strength but high thermal shock resistance to AT. Following isothermal-ageing in air at 1000°C for 14 h, both needle-like and angular particles could be seen to form on the surface of Al_2TiO_5 grains [19]. Based on the energy dispersive spectrocopy (EDS) results [19], 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 both temperature and time dependent.
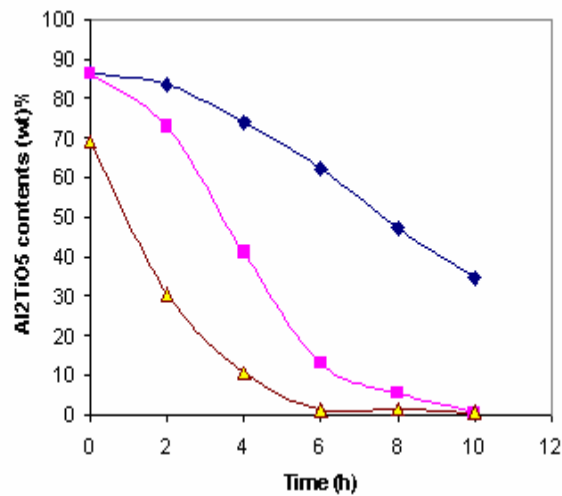

Fig. 1: Effect of Al_2TiO_5 grain size on the propensity of isothermal decomposition at 1100°C in air. [Legend: Coarse (♦); Medium (■); Fine (▲)]
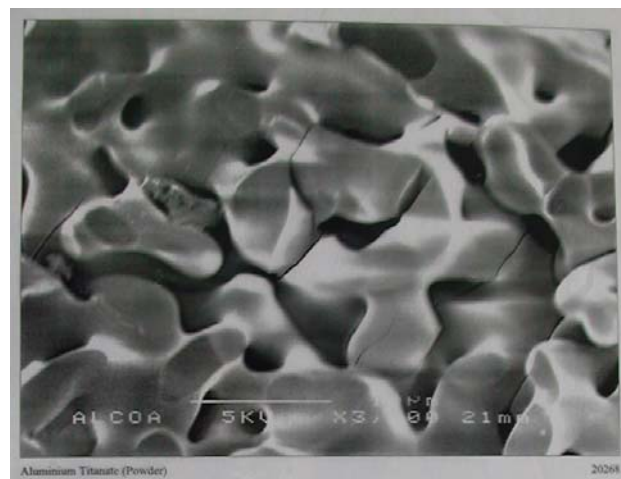

Fig.2: Scanning electron micrograph of as-sintered medium-grained AT. Note the presence of microcracks within certain grains.

Effect of Controlled Atmospheres

Figure 3 shows the isothermal stability of Al_2TiO_5 at 1100°C in air for 12 h duration. The sample remained fairly stable with no apparent phase decomposition for up to 5 h. Further ageing caused only ~5% decomposition. In contrast, substantial phase decomposition was observed when Al_2TiO_5 was aged in an argon atmosphere (Fig. 4) where more than 98% of the sample decomposed to form corundum (Al_2O_3) and rutile (TiO_2) after only 5 h of ageing. When the ageing atmosphere was changed to 50% argon and 50% oxygen (Fig. 5), the decomposition rate was considerably reduced compared with the rate for 100% argon but more substantial than the rate for air.

A closer look at the results in Figs. 3-5 suggests that the propensity of phase decomposition of Al_2TiO_5 is dependent on the atmosphere or oxygen partial pressure during isothermal ageing. This implies that the oxygen partial pressure in the atmosphere plays a key role in triggering the thermal instability via oxygen nonstoichiometry changes and/or disordering of cations in Al_2TiO_5 [6]. Indeed, nitrogen atmosphere has also been observed to cause enhanced thermal instability in Al_2TiO_5 [20].

Similar observations have also been observed for the enhanced dissociation of Ti_3SiC_2 in vacuum and argon which can also be attributed to the role of oxygen partial-pressures [21,22].
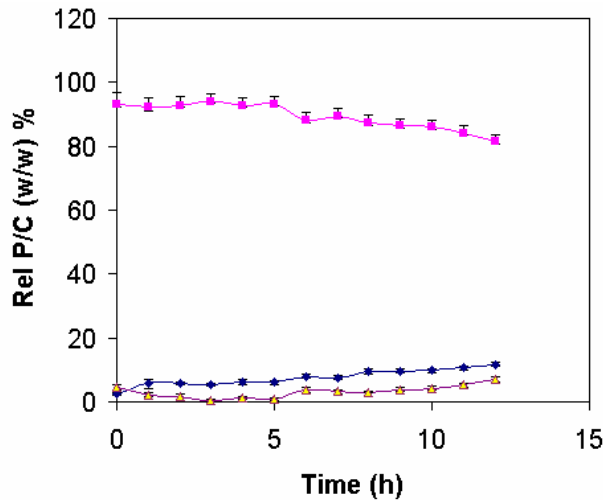

Fig. 3: Isothermal stability of Al_2TiO_5 at 1100°C in air. Errors bars indicate two estimated standard deviations ±2σ. [Legend: ■ = Al_2TiO_5; ♦ = Al_2O_3; Δ = TiO_2]
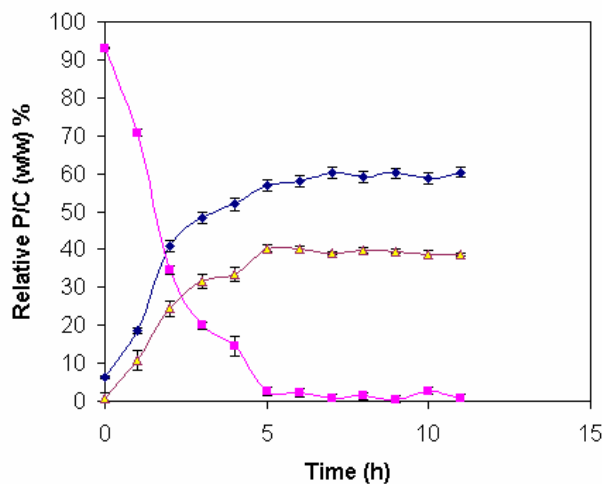
Fig. 4: Isothermal stability of Al_2TiO_5 at 1100°C in controlled argon atmosphere. Errors bars indicate two estimated standard deviations ±2σ. [Legend: ■ = Al_2TiO_5; ♦ = Al_2O_3; Δ = TiO_2]

It is postulated that in the presence of very low oxygen partial pressure, the titanium ions in TiO_2 are very susceptible to non-stoichiometry, thus triggering the release of oxygen atoms and the concomitant decomposition process. However, the exact mechanism of enhanced phase decomposition in argon or inert atmosphere remains unclear, especially in relation to the role of oxygen partial pressures in reducing the free energy change for thermal decomposition of Al_2TiO_5. If the oxygen partial pressure is the cause, then the decomposition rate of Al_2TiO_5 should depend on the variation of the oxygen partial pressure as indicated in Figs. 3 - 5. It follows that an increase in the oxygen partial pressure should reduce the rate of decomposition and vice-versa. This further implies that the thermal stability of Al_2TiO_5 will be improved in an atmosphere of 100% oxygen when compared to ageing in air.

The thermal stability of Al_2TiO_5 in the temperature range 20 – 1400°C in argon is shown in Fig. 6. Clearly, Al_2TiO_5 was stable up to ~1100°C and became unstable at between ~1150 - 1300°C. Beyond 1300°C, the thermal decomposition was arrested and the phase stability was restored. This implies that the process of thermal decomposition is reversible or recoverable provided the restricted temperature range of between ~1150 - 1300°C is not transgressed. 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. Interestingly, the use of either air, argon or oxygen atmosphere did not appear to alter the on-set temperature and the temperature range of thermal decomposition, although the propensity of phase decomposition was dramatically affected [8]. The reason for this phenomenon is unclear at this stage. To the best of our knowledge, this is the first time that the in-situ display of the temperature range for thermal decomposition of Al_2TiO_5 during ageing in controlled atmospheres as shown in Fig. 5 has been reported in the literature.
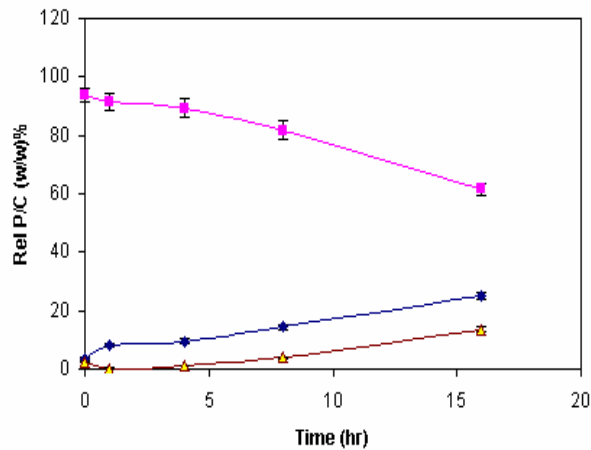

Fig. 5: Isothermal stability of Al_2TiO_5 at 1100°C in the controlled atmosphere of 50% oxygen and 50% argon. Errors bars indicate two estimated standard deviations ±2σ. [Legend: ■ = Al_2TiO_5; ♦ = Al_2O_3; Δ = TiO_2]
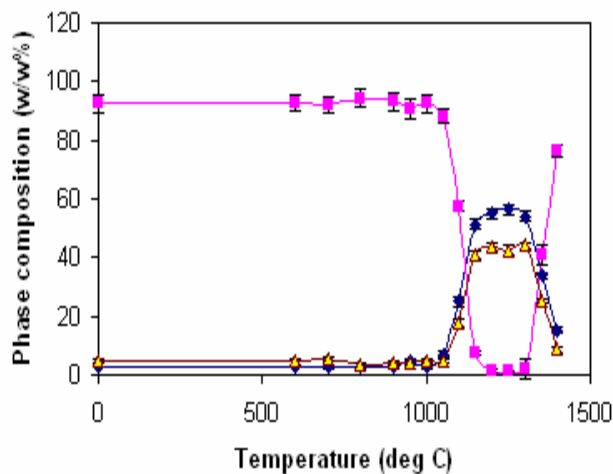

Fig. 6: Thermal stability of Al_2TiO_5 in controlled argon atmosphere over the temperature range 20 – 1400°C. Note the display of pronounced thermal decomposition at ~1150 - 1300°C. Errors bars indicate two estimated standard deviations ±2σ. [Legend:■ = Al_2TiO_5; ♦ = Al_2O_3; Δ = TiO_2]

CONCLUSION

The effects of grain size and controlled furnace atmospheres on the thermal stability of Al_2TiO_5 at 1100°C and 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 and oxygen partial pressure increases. The susceptibility of Al_2TiO_5 to thermal decomposition increases as the oxygen partial pressure of the furnace atmosphere decreases. However, neither the on-set temperature nor the temperature range of thermal decomposition is affected by the variation of oxygen partial pressure present in controlled furnace atmospheres.

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