

An Initial Study, the Effect of MgO Addition on Some Physical Properties of Al₂TiO₅

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Abstract—Aluminium titanate (Al₂TiO₅) ceramics has excellent refractory properties such as high melting point, low thermal conductivity and good thermal shock resistance. However, instability of Al₂TiO₅ phase and low mechanical strength limit the usage of this material. Some additives are used to overwhelm these problems. In this study, the effects of MgO additions (1.25, 2.5, 5 and 10 by wt. %) on the mechanical strength, bulk density and phase composition of Al₂TiO₅ ceramics was investigated. Equimolar mixtures of Al₂O₃ and TiO₂ with MgO additions were mixed in ethanol medium and samples were formed with uniaxial pressing at 60 MPa with solid-state sintering 1450 °C for 3 hours. The densities of the samples were determined by Archimedes method, mechanical strengths by three-point bending test, and phase contents by XRD. It was found that the addition of 2.5 wt. % MgO increased the strength of Al₂TiO₅ ceramics by about three times.

Keywords— Al₂TiO₅, Mechanical Properties, Refractory Ceramics, Sintering.

I. INTRODUCTION

Aluminium titanate (Al₂TiO₅) is a refractory ceramic material, produced by equimolar mixture of Al₂O₃ and TiO₂ has great potential on high temperature applications. AT ceramics has superior properties, such as high melting point (1860 °C), low thermal conductivity (~1.5 Wm⁻¹K⁻¹), good thermal shock resistance and resistance to molten aluminum corrosion [1-2]. It is used at molten aluminum industry as a riser tube. There are problems limits the usage of this material.

The first problem is the poor mechanical strength. Micro-crack formation occurs during sintering due to the high anisotropy of thermal expansion coefficients of three crystallographic axes. Moreover, Al₂TiO₅ has a pseudobrookite type crystal structure with a theoretical density of 3.70 g/cm³. The starting materials α-Al₂O₃ and TiO₂ has densities of 3.99 and 4.25 g/cm³, respectively. Therefore, formation of Al₂TiO₅ causes % 11 volume increase [3].

The second problem is the instability of Al₂TiO₅ phase. Al₂TiO₅ phase tends to decompose with in the temperature range of 800 and 1300 °C [4]. The reason of the decomposition is the collapse of the adjacent Al³⁺ (0.54 Å) and Ti⁴⁺ (0.67 Å) octahedra because the lattice sites occupied by the Al³⁺ ions are too large. The thermal energy available from this collapse allows Al³⁺ to migrate, resulting in structural dissolution to rutile and corundum [5].

In order to overwhelm these problems and improve Al₂TiO₅ ceramics properties, researchers have done much work on formation of solid solutions with oxide additives such as MgO or Fe₂O₃ in to the system which are isomorphous with the mineral pseudobrookite [6-9]. SiO₂, ZrO₂, ZrTiO₄ or Mullite is also used to strengthen Al₂TiO₅ ceramics. These additives do not form solid solutions with Al₂TiO₅ but inhibit the tendency of Al₂TiO₅ decomposition [10-11].

In the present work, the effects of MgO additions (1.25, 2.5, 5 and 10 by wt. %) on the mechanical strength, bulk density, and phase composition of Al₂TiO₅ ceramics was investigated.

II. EXPERIMENTAL PROCEDURE

The raw materials were α-Al₂O₃ (>99.7%, 2 μm, Nabaltec), rutile-TiO₂ (>98%, 0.19 μm, TRONOX® 8400), and MgO (>98%, Merck). For the mixtures investigated α-Al₂O₃:TiO₂ rutile was stoichiometric, and the quantity of MgO additive was 1.25, 2.5, 5, and 10% by mass. Powders were mixed in ball mill with porcelain balls using ethanol, and then slurries were dried in an oven at 80 °C for 24 hours. The mixed powders were formed into pellets (diameter of 30 mm and 10 mm thickness) and rectangular bars (80 mm × 15 mm) by uniaxial semi-automatic press with 60 MPa pressure. Subsequently, the green samples were sintered at 1450 for 3 hours in air to obtain dense samples. The amount of additives and sample names are listed in Table 1.

A powder diffractometer with Cu Kα radiation (λ=1.5418 Å) and a secondary graphite monochromator were used for the mineralogical analysis. XRD spectra were obtained by scanning from 15° to 70° angles (2θ), with a goniometer speed of 1.25°/min, 40 kV acceleration voltage and 30 mA current.

The bulk density and apparent porosity of the sintered samples were measured with the Archimedes method. The mechanical strengths of the samples were measured by three-point bending on a computer controlled electronic universal testing machine (Shimadzu, Japan).

TABLE I
MGO RATIO IN THE EQUIMOLAR MIXTURE OF AL₂O₃ AND TiO₂.

Sample name	MgO ratio (wt. %)
AT	-
M1	10
M2	5
M3	2.5
M4	1.25

III. RESULTS AND DISCUSSION

Figure 1 shows the bulk density of the sintered samples with different MgO contents. As it can be seen, MgO content has significant effect on the bulk density. The theoretical density of Al₂TiO₅ is 3.70 g/cm³. Adding 10 wt. % MgO increased the bulk density 3,27 to 3,47 g/cm³. This explains the formation of Al₂TiO₅ phase and depletion of the starting materials. Adding 2.5 and 5 wt. % MgO has not much effect and both bulk density and apparent porosity. Adding 1.25 wt. % MgO considerably decreased the bulk density and increased the apparent porosity of the samples. Despite the promotion of the Al₂TiO₅ solid solution formation, 1.25 wt. % MgO addition increased the apparent porosity and decreased the bulk density of the samples. To explain this change, phase content of the samples should be considered.

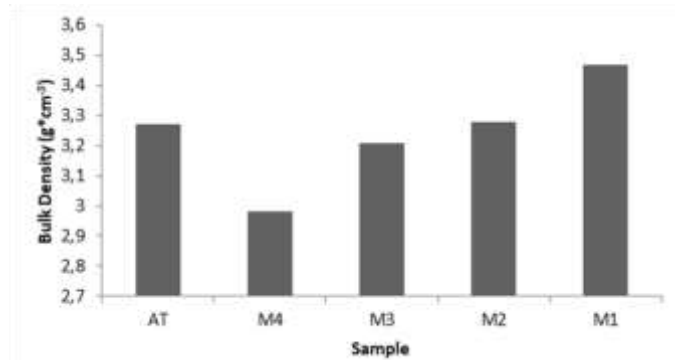


Fig. 1 Bulk density of the sintered samples

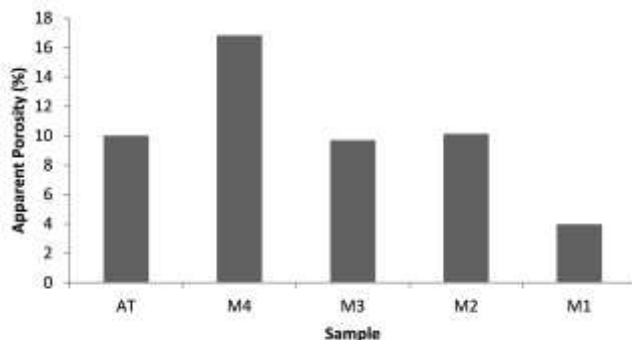


Fig. 2 Apparent porosity of the sintered samples

Figure 3 shows the XRD patterns of the sintered samples with changing the MgO amount. All samples without M4 contained unreacted α -Al₂O₃. Un-doped sample (AT) contained unreacted Al₂O₃ and TiO₂, and Al₂TiO₅. As the MgO amount increased, the Al₂TiO₅ peaks became more sharp and intensive, which means Al₂TiO₅ grains became more crystallized. MgAl₂O₄ spinel phase formed and TiO₂-rutile peaks disappeared with just adding 1.25 wt. % MgO. As the MgO content increased MgAl₂O₄ peaks became stronger. Sample M4 composed of only Al₂TiO₅ and MgAl₂O₄ phases. The Al₂TiO₅ peak at 62 to 64° shifted toward lower 2 θ values as the MgO amounts were increased. The peak shift indicates the formation of Al₂TiO₅ solid solution containing MgO, which resulted in lattice expansion [12]. MgO addition promotes the formation of Al₂TiO₅ and decreases formation temperature of Al₂TiO₅. Also, it stabilizes solid solution of Al₂TiO₅ pseudobrookite phase.

Figure 4 shows the three-point bending strengths of the samples. Addition of MgO increased the strength with formation solid solution of Al₂TiO₅. When MgO exceeds its solubility in Al₂TiO₅, it forms MgAl₂O₄. It is well known that formation of MgAl₂O₄ at the grain boundaries limits the grain growth of Al₂TiO₅ and increases mechanical properties. Despite of increase at the bulk density and decrease of the apparent porosity with addition of MgO, mechanical properties of sintered samples did not increased after adding 2.5 wt. %. The problem was macro-crack formation after sintering of the samples due to densification inhomogeneity arising from uniaxial pressing. Cold isostatic pressing could be a solution to produce more dense and homogenous samples without cracks.

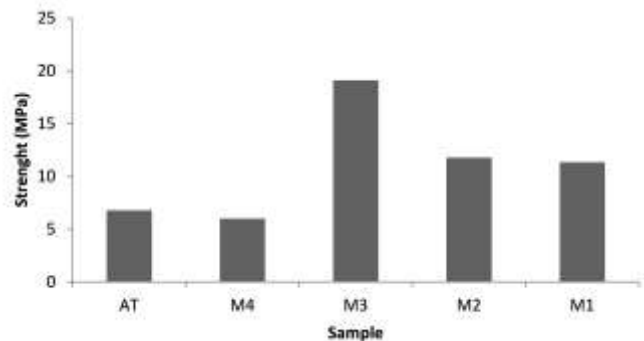


Fig. 4 Fracture strength of the sintered samples

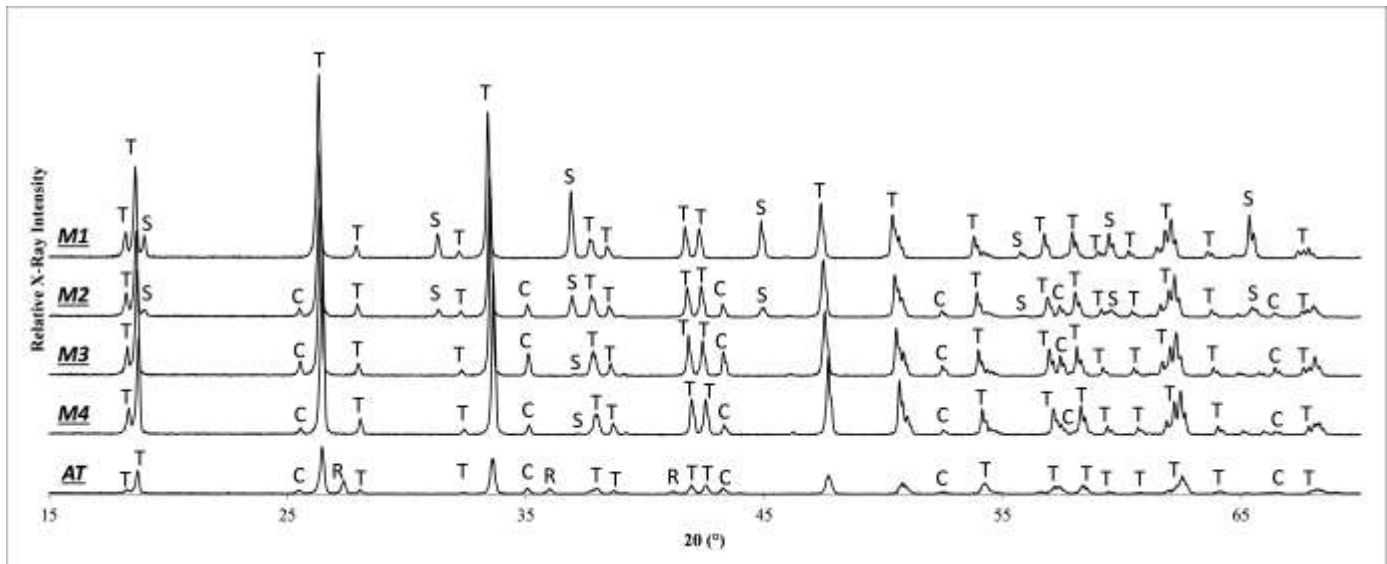


Fig. 3 X-ray diffraction patterns of the sintered samples: AT, M1, M2, M3 and M4. T is Al_2TiO_5 , C is $\alpha\text{-Al}_2\text{O}_3$, R is TiO_2 -rutile and S is Mg_2AlO_4 spinel

IV. CONCLUSION

In this study, MgO-doped Al_2TiO_5 ceramics were produced from $\alpha\text{-Al}_2\text{O}_3$, TiO_2 -rutile and MgO. MgO promoted formation of Al_2TiO_5 and increased strength with the minimum addition of 2.5 wt. %.

2.5 wt. % MgO addition formed MgAl_2O_4 spinel and increased the three-point bending strength of the Al_2TiO_5 ceramics by nearly three times.

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