

The effect of talc on the reaction sintering, microstructure and physical properties of Al_2TiO_5 based ceramics

Golsa Naderi^a, Hamid Reza Rezaie^{b,*}, Ali ShokuhFar^a, Rahim Naghizadeh^b and S. Atashgar^b

^aDepartment of Mechanical Engineering, Khajeh Nasireldin University of Iran, Iran

^bDepartment of Material Engineering, Iran University of Science and Technology, Iran

Tialite (Al_2TiO_5) is a ceramic material of very low thermal expansion coefficient, excellent thermal shock resistance, high refractoriness and good corrosion resistance. However, industrial applications of this material are hindered by two major limitations: decomposition to its parent oxides, alumina and rutile between 800 and 1280 °C and its low thermal mechanical properties. In the present study addition of talc with a good stabilizing effect has been studied on aluminum-titanate (tialite)-based ceramics. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the effect of talc on phase evolutions, sintering, and the microstructure of aluminum-titanate, and also density measurements were performed after sintering. The results showed that the presence of talc reduces the unreacted alumina and rutile significantly. The formation of $\text{Mg}_{0.3}\text{Al}_{1.4}\text{Ti}_{1.3}\text{O}_5$ and other solid solutions of MgO and aluminum-titanate were observed.

Key words: Tialite, talc, additive, MgO.

Introduction

The structure of aluminum titanate (AT) is isomorphous with the mineral psedobrookite ($\text{M}_2^{3+}\text{Ti}^{4+}\text{O}_5$) structure crystallizing with an orthorhombic space group. In this structure each Al^{3+} or Ti^{4+} cation is surrounded by six oxygen ions forming distorted oxygen octahedra. These octahedra form chains weakly bonded to each other. This structure results in the strong thermal anisotropy which creates a complicated system of localized internal stresses during cooling, causing extensive microcracking which is responsible for the mechanical weakness of the material and also for its low thermal expansion. The low thermal expansion coefficient, low thermal conductivity and high thermal shock resistance which explain the ongoing interest in this material [1-3]. Additionally this material has a very low thermal conductivity (of the order of $1.5 \text{ Wm}^{-1}\text{K}^{-1}$) and high melting point (about 1860°C) [4-6]. Tialite (Al_2TiO_5) has found applications in motor manufacture as exhaust port liners in both diesel and petrol engines as a means of improving thermal efficiency, for piston crowns, and turbo charger liners [7]. Moreover, it has found applications in the metallurgical and glass industries. However, a wider use of this material is limited by two recognized problems: First, the decomposition of Al_2TiO_5 into $\alpha\text{-Al}_2\text{O}_3$ and TiO_2 between about 800 and 1280°C. And the second problem is the very weak mechanical strength due to the thermal expansion

anisotropy-induced microcracking, this microcracking phenomenon takes place during cooling from the sintering temperature, owing to the unusually pronounced anisotropy in thermal expansion [8]. The decomposition phenomenon has been addressed through various oxide additives that form solid solutions with the aluminum titanate. The oxides that are considered to have a good stabilizing effect are Fe_2O_3 , MgO, SiO_2 , ZrO_2 , ZrSiO_4 , and La_2O_3 [9-14]. Among them, Fe_2O_3 and MgO have been considered to be the most effective ones for solving the first problem. However, a quite high percentage of MgO (of the order of 10-25 mol%) is required for an effective stabilization, and even this could not keep the material stable for more than a hundred hours at the temperature of the maximum decomposition rate (1100 °C) [14]. A solution that is proposed for the second problem is the development of composite structures including as a second phase mainly mullite, whereas zirconia and alumina have been also reported [15-19]. The present study concerns an analytical study of the effect of adding talc on tialite ceramics.

Experimental procedures

Aluminum hydroxide, $\text{Al}(\text{OH})_3$ (99.7% purity, alumina content 65%, DHM Fibrona Co, India), having a BET surface area of $1.6 \text{ m}^2/\text{g}$ and a mean particle size d_{50} of $12 \mu\text{m}$ was used as precursor for alumina. Titanium dioxide (hooks Co., purity, 98.5%) with a mean particle size of $10 \mu\text{m}$ was mixed with aluminum hydroxides in the proper stoichiometries. Talc (Luzenac 2C, France) was also added to the alumina-titania mixture at 3, 6 and 9 wt%. Table 1 summarizes the chemical composition

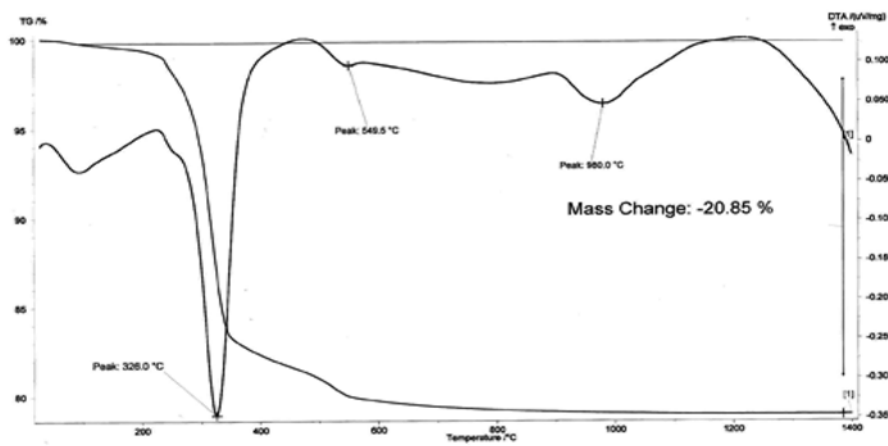
*Corresponding author:
Tel : +98-91-21025394
Fax: +98-21-77240480
E-mail: hrezaie@iust.ac.ir

Table 1. Chemical composition and the mean particle size of talc

	SiO ₂	Al ₂ O ₃	MgO	Na ₂ O	K ₂ O	CaO	Fe ₂ O ₃	TiO ₂	Particle size (d50)
Talc (wt %)	47.3	8.7	32.66	-	-	0.73	1.9	0.18	2 μ m

Table 2. Constitution of ceramic samples

Samples fired at 1200 °C	Samples fired at 1400 °C	Samples fired at 1500 °C	Samples fired at 1650 °C	Formulation
AT1	AT2	AT3	AT4	Base
3ATT1	3ATT2	3ATT3	3ATT4	Base+3%talc
6ATT1	6ATT2	6ATT3	6ATT4	Base+6%talc
9ATT1	9ATT2	9ATT3	9ATT4	Base+9%talc

**Fig. 1.** TG/DTA curves of mixed base powder.

and the mean particle size of talc. The powders were mixed in a polyethylene jar using deionized water and alumina balls for 1 h. The slurry was then dried in an oven at 120 °C for 24 h. The dried base powders were subjected to DTA and TG tests up to 1400 °C in air by a Netzsch STA 409 PC/PG instrument. In both cases, a constant heating rate of 5K.minute⁻¹ was employed and alpha alumina was used as a reference. The powder was uniaxially pressed in a steel die 20 mm in diameter at 100 MPa to form cylindrical bars followed by sintering at 1200, 1400, 1500, 1650 °C in air for 3 h with a heating rate of 5 K.minute⁻¹ and furnace cooled. Three series of ceramic samples were prepared with three different loadings of talc 3, 6 and 9 wt% and one series was made without any additive as a reference sample. The combination of samples is shown in Table 2. After comparing the properties of samples, the sample with a composition of 9 wt% doped talc after sintering was carried out using a Philips-D80 (Cu K α radiation) XRD, and the microstructure and morphology of these samples were evaluated by SEM (Cambridge S360). Furthermore, the bulk densities of all samples were measured by dipping in water.

Results and Discussion

Figure 1 shows the TG/DTA analyses of mixed base powders. The first endothermic peak at around 100 °C is

related to the removal of physical water. The sharp endothermic peak at 326 °C in the DTA pattern indicated the decomposition of the $Al(OH)_3$. Also the TG analysis confirmed that the decomposition of the $Al(OH)_3$ precursor into γ -alumina started below 300 °C and was completed at about 550 °C. Rutilization occurred above 900 °C and therefore the peak at the 980 °C can be attributed to this reaction. Subsequently, the conversion to tialite formation occurred at about 1280 °C. The XRD patterns of samples which were fired at 1200, 1400, 1500 and 1650 °C for 3 h, (AT1, AT2, AT3, AT4, 9ATT1, 9ATT2, 9ATT3, and 9ATT4 samples) are shown in Figs. 2, 3, 4 and 5 respectively. Among those samples which were fired at 1200 °C, formation of tialite is observed only in the 9ATT1 sample which was doped with talc, although sharp peaks of rutile and corundum also appeared. After firing at higher temperatures, 9ATT2, 9ATT3 and 9ATT4 samples, and unreacted rutile has not been observed, this shows that the reaction of tialite formation is completed by increasing the temperature. The presence of talc leads to weak lines from MgO and Al_2TiO_5 solid solutions with different stoichiometries such as the $Mg_{0.3}Al_{1.4}Ti_{1.3}O_5$ phase in 9ATT1 and the $Mg_{0.6}Al_{0.8}Ti_{1.6}O_5$ in 9ATT2 samples. According to literature studies, the formation of these solid solutions improves the thermal stability of tialite and the decomposition phenomenon has been addressed through

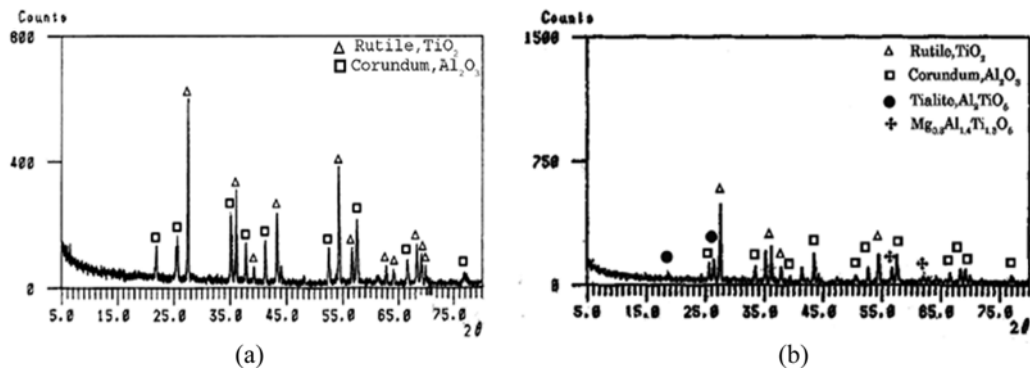


Fig. 2. XRD patterns of tialite ceramics after firing at 1200 °C, (a) tialite ceramics (AT1), (b) tialite ceramics doped with talc (9%wt) (9ATT2).

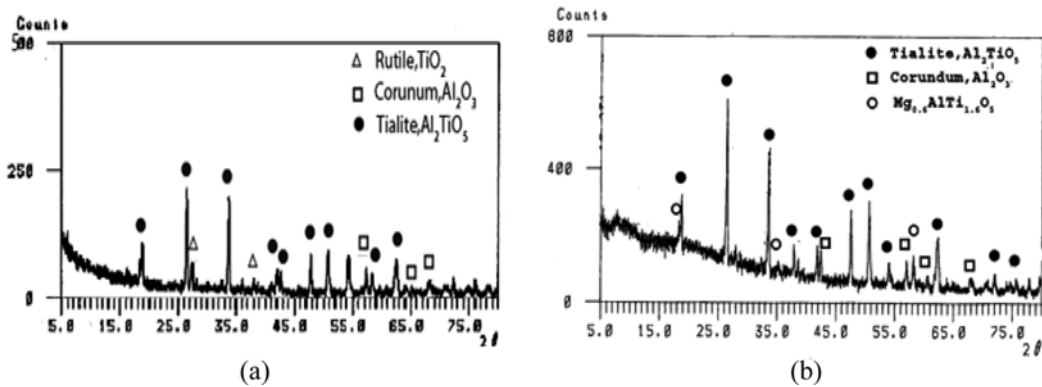


Fig. 3. XRD patterns of tialite ceramics after firing at 1400 °C, (a) tialite ceramics (AT2), (b) tialite ceramics doped with talc (9%wt) (9ATT2).

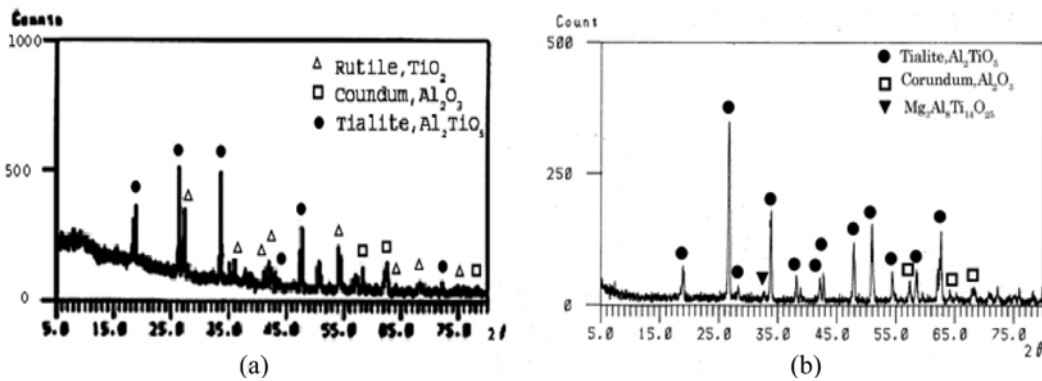


Fig. 4. XRD patterns of tialite ceramics after firing at 1500 °C, (a) tialite ceramics (AT3), (b) tialite ceramics doped with talc (9%wt) (9ATT3).

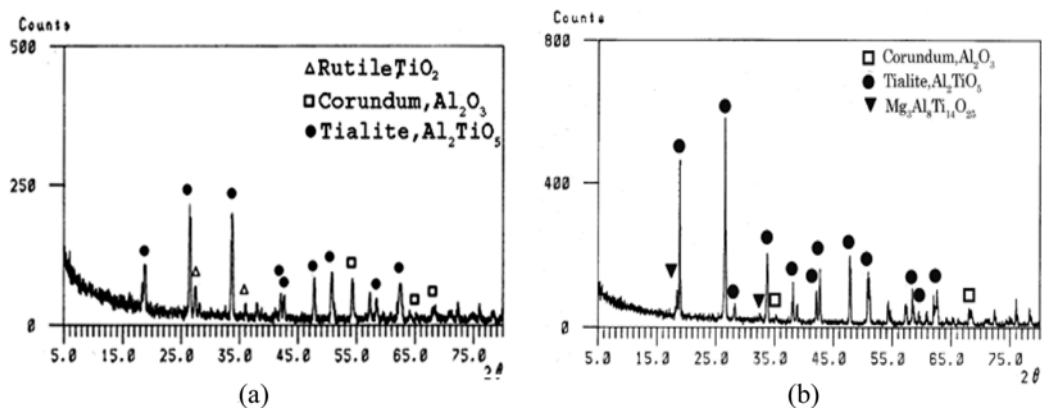


Fig. 5. XRD patterns of tialite ceramics after firing at 1650 °C, (a) tialite ceramics (AT4), (b) tialite ceramics doped with talc (9%wt) (9ATT4).

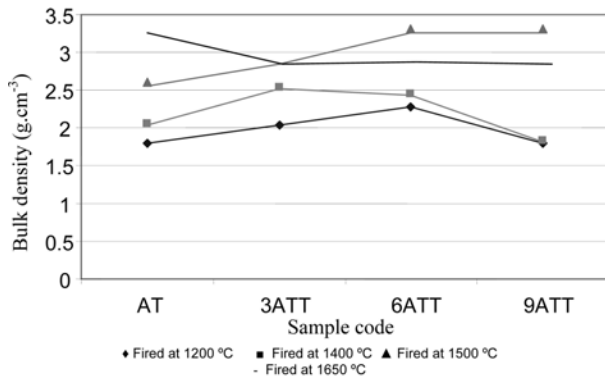


Fig. 6. The bulk densities of tialite ceramics.

various oxide additives that form solid solutions with aluminum titanate. Recently it has been recognized that the combined effects of MgO and SiO_2 , such as talc, enhance significantly the material stability [3, 14, 15]. The bulk density of samples, which were fired at four different temperatures 1200, 1400, 1500 and 1650 °C is shown in Fig. 6. These results showed an increase in bulk density with increasing temperature in the non-talc doped sample but talc-doped (6, 9%wt) samples fired at 1650 °C show a lower density in comparison with

those samples that were fired at 1500 °C, because of the large amount of tialite formation. In fact the relative density of samples decreased with increasing Al_2TiO_5 (tialite) content, the densities of the starting oxides $\alpha\text{-Al}_2\text{O}_3$ and TiO_2 (rutile) are 3.99 and 4.25 gr/cm^3 respectively, therefore, the formation of pseudobrookite type $\beta\text{-Al}_2\text{TiO}_5$ with a theoretical density of 3.79 gr/cm^3 was accompanied by an 11% increase in molar volume. With increasing talc content in tialite the samples from 6 to 9 (wt%), bulk density reduced which might be because of growing the tialite phase formation. The SEM observations of the microstructure of samples which were fired at 1400 °C are shown in Fig. 7. In all talc-doped samples compared to non-doped additive samples a homogeneous tialite microstructure is observed. Taruta et al. showed that Al_2TiO_5 particles formed by the reaction between Al_2O_3 and rutile at the junction of Al_2O_3 grains. Al_2TiO_5 particles might be nucleated on the Al_2O_3 grains and the small size of Al_2TiO_5 particles grow and contact with each other [19]. Tialite formation was not completed at this temperature and unreacted alumina and rutile were observed significantly. Generally by using EDS (Energy dispersive spectroscopy) it was found that the gray areas are the tialite grains, the white ones are rutile, the dark points

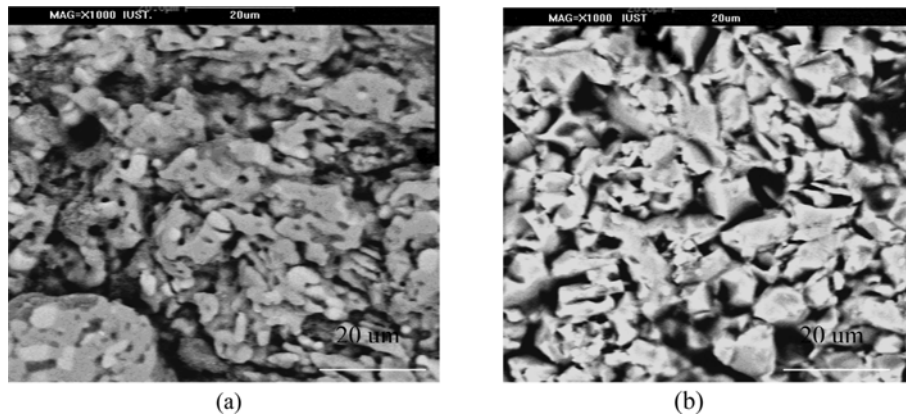


Fig. 7. SEM micrographs of tialite ceramics at 1400 °C, (a) AT2, (b) 9ATT2.

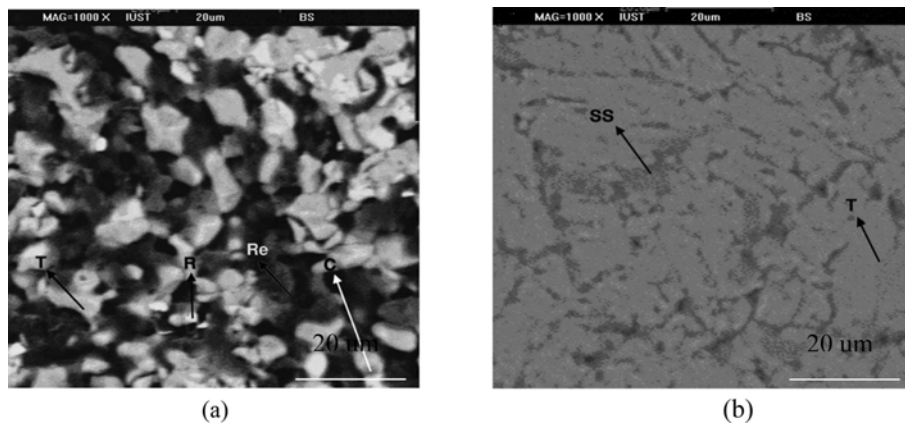


Fig. 8. SEM micrographs of tialite ceramics at 1500 °C, (a) AT3, (b) 9ATT3.

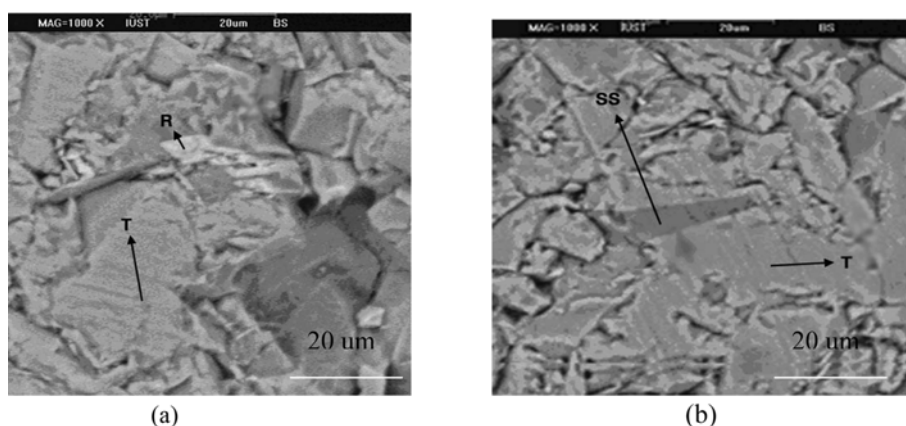


Fig. 9. SEM micrographs of tialite ceramics at 1650 °C, (a) AT4, (b) 9ATT4.

are corundum and black areas are the pores distributed uniformly throughout the matrix. Moreover adding talc at this temperature improves tialite formation and Fig. 7(b) in comparison with Fig. 7(a) shows more homogeneity. By increasing the temperature up to 1500 °C, reactions became more complete. As an interesting result, Fig. 8(a) still shows tialite phase along with a two phase structure including rutile and corundum which is indicated in the image by R and C letters respectively. In this figure some areas (the dark gray areas) are resin which remains from mounting. But by doping with talc, the structure changes to an almost single phase of tialite (sign T) with MgO and Al_2TiO_5 solid solutions with different stoichiometries such as $\text{Mg}_{0.3}\text{Al}_{1.4}\text{Ti}_{1.3}\text{O}_5$ and $\text{Mg}_{0.6}\text{Al}_{0.8}\text{Ti}_{1.6}\text{O}_5$ phases (sign SS), Fig. 8(b). By using EDS the presence of solid solutions of tialite and MgO with different stoichiometries in talc doped samples was determined and pointed to by the sign SS, in Fig. 8(b). After sintering at 1650 °C although the amounts of unreacted oxides in AT4 samples in comparison with other non-talc doped samples are minimized, there are some light areas which represent unreacted rutile, which is shown by R in this figure. In talc-doped samples (9ATT4) sintered at the same temperature, 1650°C, tialite formation became complete and no rutile has been left, Fig. 9(b). By using EDS the presence of solid solutions of tialite and MgO with different stoichiometries in 9% talc-doped samples was determined and pointed to by the sign SS, in Fig. 9(b).

Conclusions

Tialite ceramics were prepared and the effect of using talc as an additive was investigated. The conclusions derived are summarized as follows:

- A talc addition leads to the production of a low quantity of tialite, at 1200 °C and complete formation of tialite at 1400 °C.

- In the talc-doped samples a tialite phase was observed and solid solutions of MgO and tialite determined inside tialite grains.

- With increasing temperature, up to 1650 °C tialite formation was complete.

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