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The effect of Fe_2O_3 addition on tialite formation

H.R. Rezaie [*], R. Naghizadeh, N. Farrokhnia, S. Arabi, M. sobhani

Department of Engineering Materials, Iran University of Science & Technology, Iran

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Abstract

Aluminium titanate (Al_2TiO_5) exhibits interesting properties, such as low thermal expansion, high thermal shock resistance, high refractoriness, and good corrosion resistance. In this research, effect of hematite (Fe_2O_3) addition on the formation temperature of Al_2TiO_5 was studied starting from very fine (micronsized) rutile (TiO_2) and aluminum hydrate ($Al(OH)_3$) powders. Samples with (0, 2.5, 5, 7.5, and 10) wt.% hematite were prepared for comparison. Identification of phases was accomplished using X-ray diffraction. The samples were characterized by simultaneous thermal analysis and microstructural analysis using scanning electron microscopy. The addition of Fe_2O_3 changes the mechanism of tialite formation. The main results are reduction in tialite formation temperature down to 1150 °C, tialite grains growth, and decrease of porosity.

Keywords: Aluminum titanate; Fe_2O_3 additive; Formation

1. Introduction

Aluminum titanate (Al_2TiO_5), generally obtained by a solid-state reaction between Al_2O_3 and TiO_2, has a very low thermal expansion coefficient (0.2×10^{-6} to 10^{-6}) [1] low thermal conductivity (0.9–$1.5\ \mathrm{Wm^{-1}\,K^{-1}}$), and a high thermal shock resistance [2,3]. These properties make it suitable to be used most in components of internal combustion engines, as insulating coating, electronical and high temperature electrical part components, molten glass and metal thermometer components. The crystal structure of aluminium titanate is orthorhombic with lattice parameters of: $a = 35.91$, $b = 94.29$, and $c = 96.36$ nm. That thermal expansion coefficient is positive along a and b crystal directions and negative along c axis [4], creates a prominent thermal expansion anisotropy which tends to a very low thermal expansion, beside microcracks, makes it difficult to obtain high strength in room temperature. Microcracks depend strongly on microstructure [5]. Below the critical grain size, during cooling system elastic energy is insufficient for forming microcracks, thus mechanical properties improve conspicuously [1,6], what mentioned as critical grain size depends on sample's thermal history and it is about 1–2 μm [7]. Another problem which represents serious limitation to utilization of aluminium titanate is the tendency to decompose to Al_2O_3 and TiO_2 in the range 750–1300 °C. Aluminium titanate exists in two allotropic forms, α and β. The low-temperature phase β-Al_2TiO_5, has two temperature ranges of stability, the first from room temperature up to around 750 °C, and the second from 1280 °C up to the inversion temperature at 1820 °C [8]. The high-temperature phase, α-Al_2TiO_5, is stable from 1820 °C up to the melting temperature (1860 °C). Conventionally, formation of tialite proceeds according to the following endothermic reaction in temperatures over eutectoid temperature of 1280 °C [8,9].

$$\alpha\text{-}Al_2O_3 + TiO_2(\text{rutile}) \rightarrow \beta\text{-}Al_2TiO_5 \qquad (1)$$

Yet the product of this reaction is a porous body in which the formation reaction is not complete and it can be used as a starting material in later production process [10]. To overcome this problem using monosized oxide powders [11], preparation through organo-metallic precursors [12], and employing additives are common [3]. The molar free energy of Al_2TiO_5 formation can be estimated by a third-law treatment of the available heat capacity data [13,14] and the equilibrium temperature [9], and it has been confirmed experimentally.

$$\Delta G^{\circ}_{Al_2TiO_5} = \Delta H^{\circ} - \Delta S^{\circ} T = 17000 - 10.95T$$
$$= -10.95\Delta T(\mathrm{J/mol})$$

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[*] Corresponding author. Tel.: +98 2173912856; fax: +98 2177240480.
E-mail address: hrezaie@iust.ac.ir (H.R. Rezaie).

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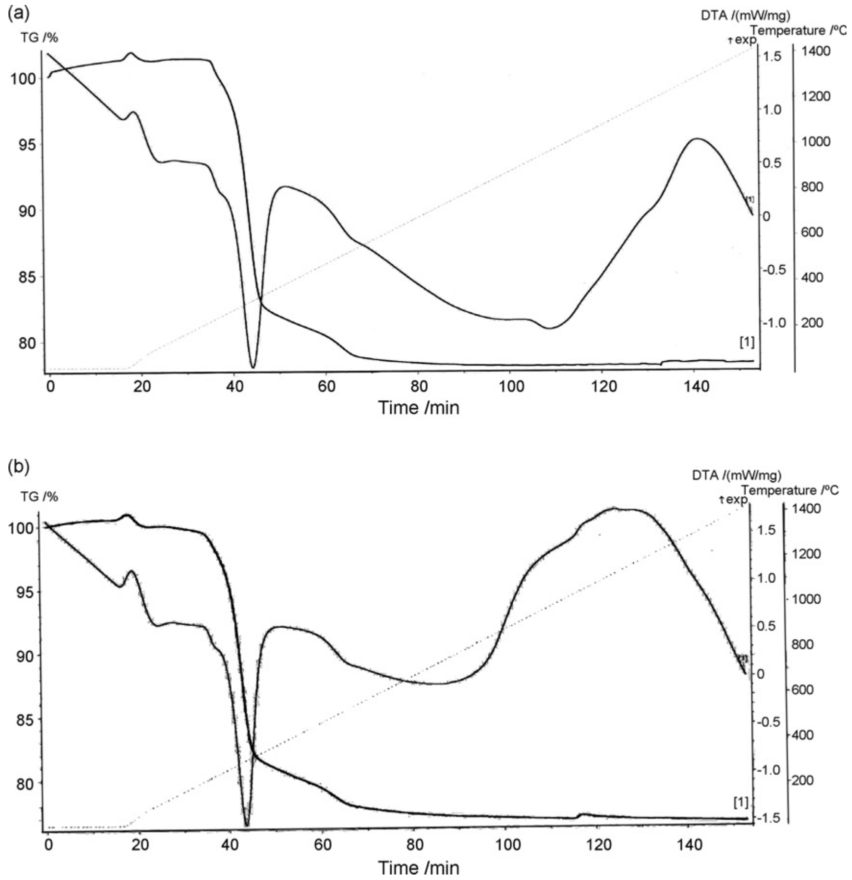

Fig. 1. STA curves of specimens containing (a) 0 and (b) 5 wt.% of Fe_2O_3.

where $\Delta T = T - 1553$ (K) [15]. Tialite formation process was precisely examined by Freudenberg and Mocellin [16,17]. They insisted on the importance of the new phase nucleation and growth in developing the final microstructure in the range 1280–1400 °C. The crystal structure of β-Al_2TiO_5 is of the pseudobrookite type [4,18] with a theoretical density of 3.70 g/cm^3 [18].

The density of the starting oxides, α-Al_2O_3 and TiO_2 (rutile) are 3.99 and 4.25 g/cm^3 respectively. Therefore, reaction (1) is accompanied by an 11% volume increase bringing problems during sintering [17,19].

2. Experimental procedures

To form tialite, commercially available $Al(OH)_3$ (DHM, fibrona, India, aluminum hydrate, $d_{50} = 12$ μm) and TiO_2 (Hooks Co., China, purity 98.5%) were weighed in appropriate stoichiometery and 2.5, 5, 7.5, and 10 wt.% hematite (Fe_2O_3, Iranian Co., purity 99%) powder was added to the mixture. The compositions were homogenized in an alumina ball-mill using alumina balls as milling media for 1 h. The slurries sieved to 300 mesh, dried and again sieved. After that, the mixture with 0.1 wt.% binder (PVA) (dry base) was pressed uniaxially under pressure of 4 bar to form discs of 15 mm diameter then subjected to drying at 110 °C for 24 h. Powders with 0 and 5 wt.% Fe_2O_3 were characterized by Simultaneous thermal analysis (NETZSCH STA 409 PC/PG). To investigate the influence of Fe_2O_3 on the formation temperature of Al_2TiO_5, specimens were heated in air with a heating rate of 5 °C/min at 1150, 1250, 1350, and 1450 °C with soaking time of 5 h and then cooled in the furnace overnight. X-ray analysis (XRD, Jeol 8030 diffractometer) was performed using Cu Kα radiation. Weight percent (%wt) of phases available in the specimens were determined by XRD analysis results. The calibration coefficients of every phase were calculated by help of peak intensity of two standard samples, first one containing the $Al(OH)_3$ and TiO_2 powders and the second tialite powder syntesized at 1350 °C and TiO_2 powder according to following equation:

$$\%\mathrm{wt}_{\mathrm{Tialite}} = \frac{A.I_{\mathrm{Tialite}}}{A.I_{\mathrm{Tialite}} + B.I_{\mathrm{Rutile}} + C.I_{\mathrm{Corundum}}} \qquad (2)$$

where I_{Tialite}, I_{Corundum}, and I_{Rutile} are respectively peak intensity of tialite (1 0 1), corundum (1 1 3), and rutile (1 1 0) reflections [20]. A, B and, C represent calibration coefficients of tialite, corundum and rutile, respectively. The microstructure of samples fired at 1250 and 1450 °C was observed by scanning electron microscope (SEM, Cambridge S-360 Model), after mounting and metallographic preparations. The backscattered (BS) mode was especially useful in detecting the presence of unreacted particles, and investigation of phases.

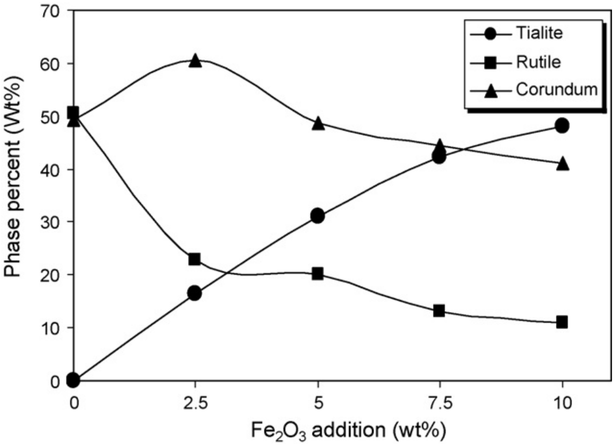

Fig. 2. Phase percentage variation with Fe_2O_3 contents at 1150 °C.

3. Results and discussion

3.1. STA analysis

STA curves of samples containing 0 and 5 wt.% of Fe_2O_3 are shown in Fig. 1(a and b).

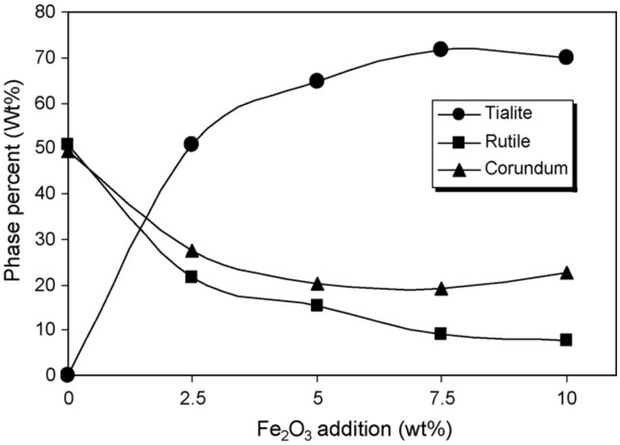

Fig. 3. Phase percentage variation with Fe_2O_3 contents at 1250 °C.

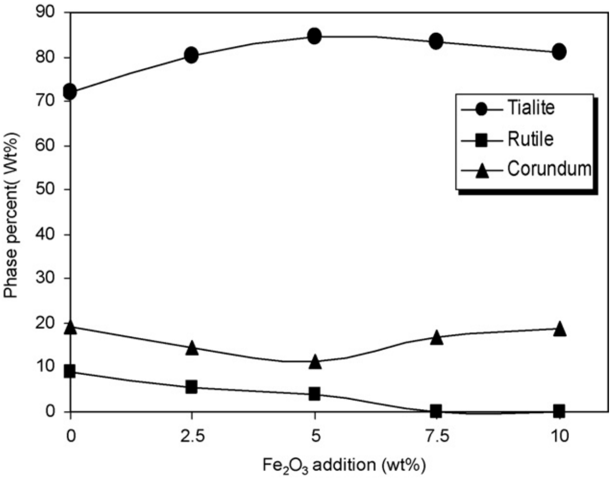

Fig. 4. Phase percentage variation with Fe_2O_3 contents at 1350 °C.

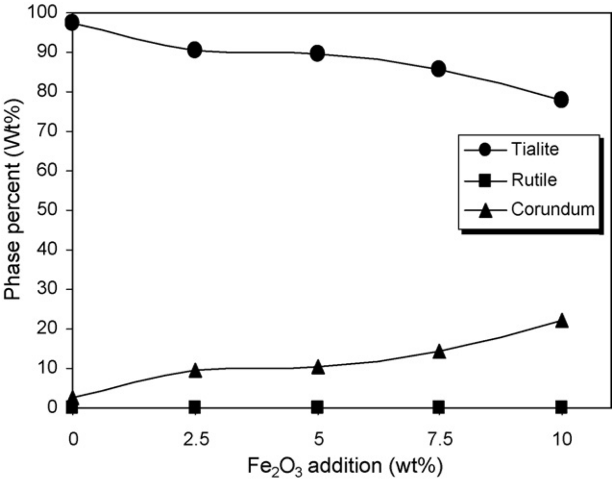

Fig. 5. Phase percentage variation with Fe_2O_3 contents at 1450 °C.

As it is seen in this figure (a and b) with addition of Fe_2O_3 the peak width of tialite formation is increased whereas the formation temperature of tialite decreased to the lower temperatures.

3.2. X-ray diffraction analysis

Weight percent of tialite, curundum and rutile at different temperatures are shown in Figs. 2–5. As can be seen in Fig. 2, the phases in specimens not containing Fe_2O_3, fired at 1150 °C are only corundum and rutile, whereas no tialite phase is detected. It indicates that corundum and rutile remain unreacted. By additional of Fe_2O_3 tialite peaks appeared in XRD curves, as mentioned before, formation temperature of tialite produced from solid-state reaction between TiO_2 (rutile)

Table 1
Lattice parameters of tialite with different amounts of Fe_2O_3 additive

Sintering temperature (°C)	Additive (wt.%)	Tialite Lattice constants (nm)		
		a	*b*	*c*
1150	0	–	–	–
	2.5	9.480	9.892	3.608
	5	9.472	9.687	3.597
	7.5	9.492	9.646	3.596
	10	9.412	9.684	3.595
1250	0	–	–	–
	2.5	9.452	9.665	3.598
	5	9.354	9.648	3.573
	7.5	9.412	9.668	3.595
	10	9.614	9.737	3.640
1350	0	9.314	9.635	3.569
	2.5	9.276	9.590	3.548
	5	9.412	9.572	3.547
	7.5	9.314	9.652	3.569
	10	9.452	9.681	3.598
1450	0	9.432	9.627	3.593
	2.5	9.432	9.643	3.587
	5	9.492	9.678	3.608
	7.5	9.472	9.687	3.610
	10	9.492	9.694	3.608

and α-Al_2O_3 is over the eutectoid temperature of 1280 °C [4], thus presence of tialite in samples containing additives fired at 1150 °C proves the noticeable effect of Fe_2O_3 in decreasing the formation temperature of tialite. By increasing the weight percent of added Fe_2O_3, the amount of tialite is increased and the amount of rutile is decreased. That is a sign of improvement in tialite formation. Raising the firing temperature up to 1250 °C, only corundum and rutile are apparent phases in specimens not containing Fe_2O_3 (Fig. 3). Again, by addition of Fe_2O_3, tialite phase is observed at 1250 °C. There is an increase of tialite formation with increasing the amount of Fe_2O_3%. The amount of tialite comparing to that in specimens fired at 1150 °C is significant. Since 1350 °C is over the eutectoid temperature (1280 °C), XRD patterns of samples not containing Fe_2O_3 fired at 1350 °C show tialite as the major phase and, rutile and corundum as minor phases (Fig. 4). By increasing the Fe_2O_3 in samples, the ultimate amount of tialite phase increases while rutile shows the reverse. In samples containing 7.5 and

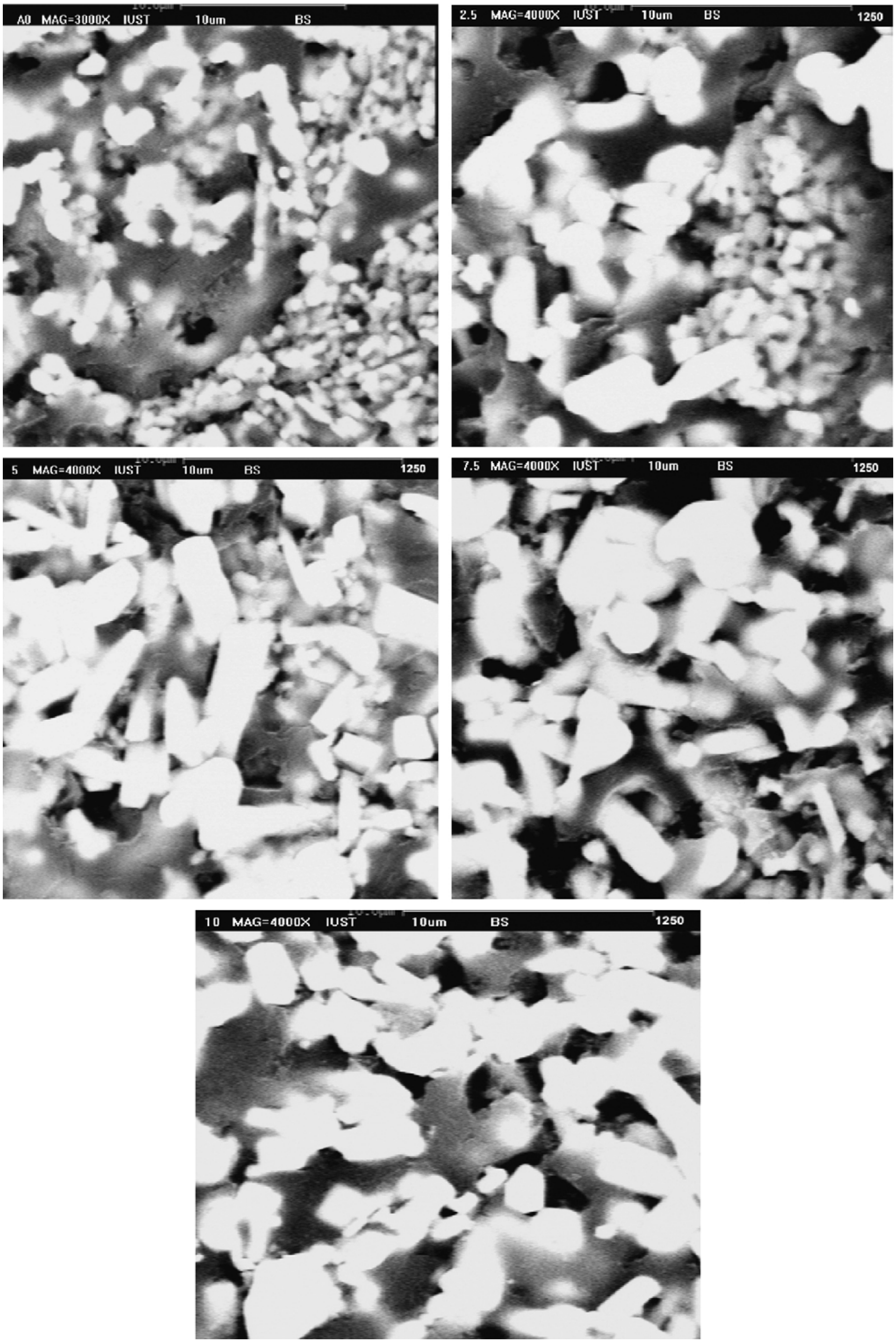

Fig. 6. BS images of specimens fired at 1250 °C for 5 h with different amounts of Fe_2O_3.

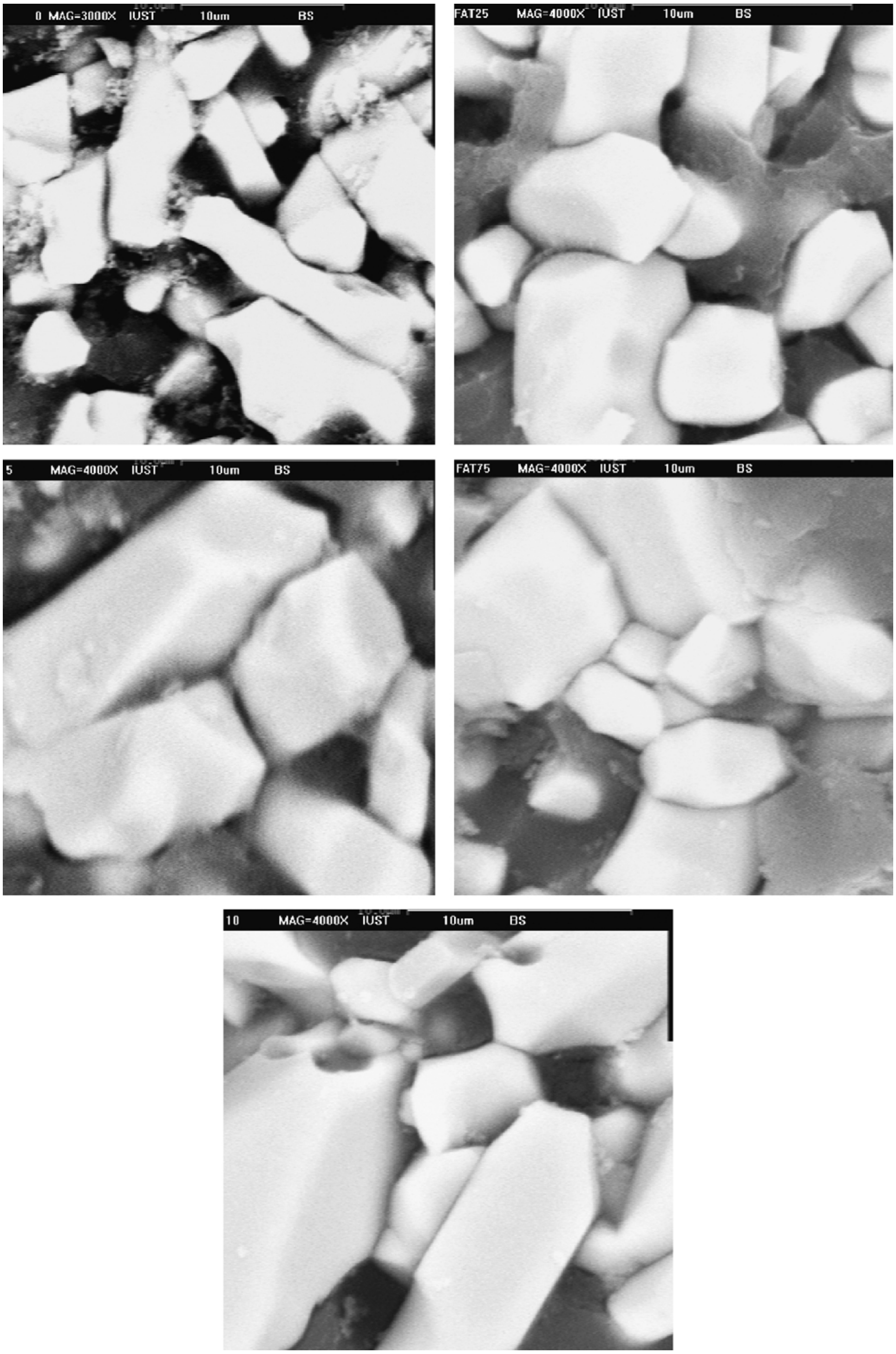

Fig. 7. BS images of specimens fired at 1450 °C for 5 h with different amounts of Fe_2O_3.

10 wt.% Fe_2O_3, the amount of rutile is zero which shows the completion of formation process. Presence of corundum in samples is probably the result of the reaction between Fe_2O_3 and TiO_2 to form Fe_2TiO_5 solid solution. Trivial amount of corundum remained in samples not containing additive is considered as lack of stoichiometery in starting powders or impurities entered during ball-milling process.

Fig. 5 shows that tialite formation process completes at 1450 °C and the original phase of all samples is tialite plus small amount of corundum as a secondary phase. In samples not containing additive the greatest amount of Al_2TiO_5 is represented though it is diminishing as more corundum is remained unreacted and more Fe_2TiO_5 solid–solution is formed while increasing the Fe_2O_3. Tialite lattice parameters were calculated via XRD results, atomic planes distance and, planes indices in orthorhombic system (Table 1). Changes in lattice parameters in the tialite are evidence of Fe_2O_3 entered tialite structure.

3.3. Microstructural studies

Back scattered (BS) images of samples which fired at 1250 °C not containing Fe_2O_3, indicate grains with inclusions of unreacted TiO_2 (tiny white spherical particles) and Al_2O_3 (light gray), beside pores of spherical shape (black) plus mounting resins (dark gray). Brittleness of samples while polishing proves the porous structure. By increasing the amounts of Fe_2O_3 tialite grains are improved, therefore unreacted oxide particles are decreased. Backscattered (BS) images were taken from samples fired at 1450 °C includes tialite as a major phase with white micron grains, dispersed gray mount resins and, black colored pores. Samples not containing Fe_2O_3 represent an inhomogeneous structure with flat grain distribution consisting of elongated plate-shaped white tialite grains in an average size of 3–10 μm. By adding Fe_2O_3 grains became bigger in size and grain size distribution became flatter. Also, the amount of porosity decreases in the beginning of the sintering process as inter particle joints are created. An explanation of this matter is that increasing the amount of Fe_2O_3, speeds the action of grain growth and formation of inter particle joints through forming a solid solution with tialite within lower temperatures. Kinetically, by means of the Fe_2O_3 entered the tialite structure and the Al_2O_3 remained from the starting mixture, preferred sites for nucleation are provided, so nucleation occurs easier and tialite grains grow (Figs. 6 and 7).

4. Conclusions

1- Addition of 2.5 wt.% Fe_2O_3 to a fine mixture of aluminum hydrate and rutile resulted in decreasing the tialite formation temperature from temperatures over 1280 °C down to 1150 °C.

2- The moderately good microstructure of Al_2TiO_5 was improved by addition of Fe_2O_3 up to 7.5% so that tialite grains became larger in size while pores were diminished.

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