

The Effects of Temperature and Additives on the Microstructure of Al_2TiO_5

Melih Özçatal¹, M. Serhat Başpınar¹

Department of Metallurgical and Materials Engineering, Afyon Kocatepe University, Afyonkarahisar, Turkey¹

ABSTRACT: Aluminum titanate (Al_2TiO_5) ceramics has superior high temperature properties such as high melting point, low thermal conductivity, and high thermal shock resistance. This study discusses the effects of temperature and doping on the microstructure of Al_2TiO_5 produced by powder metallurgy techniques. In order to determine the effects of additives 10 wt. % SiO_2 or Fe_2O_3 was used in the experiments. Samples without and with additives were sintered at 1450 and 1600 °C. The microstructural properties were characterized with scanning electron microscope (SEM). X-ray diffraction (XRD) was performed for phase identification of the samples. The study results showed that increasing sintering temperature eliminated pores and decreased the unreacted phases of rutile and corundum. Furthermore, it was observed that both additives inhibited the grain growth of Al_2TiO_5 and decreased the number of cracks.

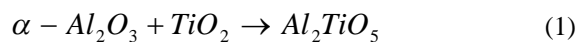
KEYWORDS: Aluminum titanate, Microstructure, Additives, Sintering.

I. INTRODUCTION

Aluminum Titanate (AT) is a synthetic ceramic material has a great potential on high temperature applications due to its high melting point (1860°C), low thermal conductivity ($\sim 1.5 \text{ Wm}^{-1}\text{K}^{-1}$) and high thermal shock resistance [1-2].

There are two drawbacks limits the industrial use of this material.

The first problem is low mechanical strength due to high micro-crack formation. The reason of micro-crack formation is high anisotropy of thermal expansion coefficients, which are -3.0, +11.8, and $+21.8 \times 10^{-6}/\text{K}$ in each of its three crystallographic axes. AT has a pseudobrookite type crystal structure with a theoretical density of 3.70 g/cm^3 . Reaction (1) shows the formation of AT. The densities of starting materials are 3.99 and 4.25 g/cm^3 . Thus, formation of AT accompanied by an 11% volume increase [3].



The second problem is the instability of AT phase. AT tends to decompose into Al_2O_3 and TiO_2 between 750-1300 °C while heating and cooling. This decomposition occurs when adjacent Al^{3+} (0.54 Å) and Ti^{4+} (0.67 Å) octahedra collapse because the lattice sites occupied by the Al^{3+} ions are too large. The thermal energy available from this collapse allows Al^{3+} to migrate, resulting in structural dissolution to rutile and corundum [4].

Various stabilizers have previously been studied from the perspective of thermodynamic and kinetic stabilization. Thermodynamic thermal stability can be increased by additions of MgO , Fe_2O_3 or TiO_2 , which have pseudobrookite structures [5-6]. Thermodynamic stabilization is related to the material's decreased decomposition temperature during cooling. AT can also be kinetically stabilized with limiting its grain growth with SiO_2 , which do not form a solid solution with AT but rather restrain the tendency of toward decomposition [7]. AT can also be stabilized with addition mullite, ZrO_2 , or $ZrTiO_4$ as a kinetic stabilization [8-10].

In this study 2 types of stabilizers were used: AT with the addition of only Fe_2O_3 and only SiO_2 . Samples were sintered at 1450 and 1600°C. The effect of additives and sintering temperature on the phase formation and microstructure are discussed.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Special Issue 12, May 2016

II. MATERIALS AND METHODS

A. Sample Preparation

Commercially available α -Al₂O₃ (corundum), TiO₂ (rutile), Fe₂O₃ (hematite) and SiO₂ (quartz) powders were used as starting materials. For the mixtures investigated α -Al₂O₃:TiO₂ rutile was stoichiometric, and the quantity of both additive materials was 10% by mass. Powders were mixed in porcelain jar and balls using water, and then slurries were dried in an oven at 105 °C for 24 hours. Then powders were again put in jar and dry mixed for 1 hour to break agglomerates. The mixed powders were formed into pellets (diameter of 30 mm and 10 mm thickness) by uniaxial semi-automatic press with 50 bars hydraulic pressure. Subsequently, the green pellets were sintered at 1450 and 1600 °C for 3 hours in air to obtain dense samples.

B. Characterization

A powder diffractometer with Cu K α radiation ($\lambda=1.5418 \text{ \AA}$) and a secondary graphite monochromator were used for the mineralogical analysis. XRD spectra were obtained by scanning from 5° to 80° angles (2 θ), with a goniometer speed of 1.25°/min, 40 kV acceleration voltage and 30 mA current.

The samples were mounted with the vacuum impregnation method and polished to have flat surfaces prior to SEM investigation. Then, they were coated with carbon and examined with SEM attached with an energy dispersive X-ray spectrometer under 20kV with 20 mm working distance (WD).

III. RESULTS AND DISCUSSION

A. XRD Analysis

Figure 1 shows the XRD spectra of the starting powders. It can be understood that powders are not containing impurities more than 5 wt. %.

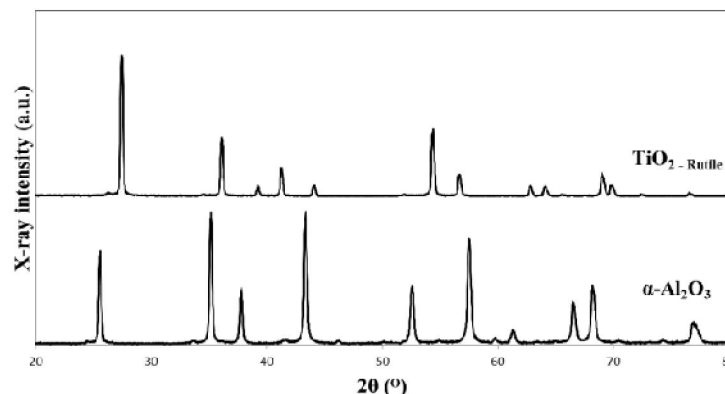


Fig.1.XRD patterns of the starting powders

In order to understand the effect of sintering temperature and the effect of Fe₂O₃ and SiO₂ additions, the samples were prepared with 10 wt.% additive and sintered 1450 and 1600°C. Specimens with additives and sintering temperatures such as Fe₂O₃, SiO₂,1450°C, 1600°C, which are denoted as AT1450, AT1600, F1450, F1600, S1450 and S1600, respectively. Figure 2 shows the XRD pattern of the sintered samples. All samples have high intensities of AT phase. Samples with no additives contain unreacted Al₂O₃ and TiO₂. This was proven with the SEM investigations (Figure 3). Samples composed of 10 wt. % hematite have also unreacted Al₂O₃ and TiO₂ phases but no Fe₂O₃. It is known that Fe³⁺ ions can enter AT structure and form a solid solution. To form a solid solution, the solute and the element that it is replacing must have a similar ionic radius and similar valance. Similar crystal structures are helpful

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Special Issue 12, May 2016

but not always necessary. Fe^{3+} with a radius of 0.64 Å, readily forms solid solutions with Al^{3+} in AT, which has a Radius of 0.54 Å [11].

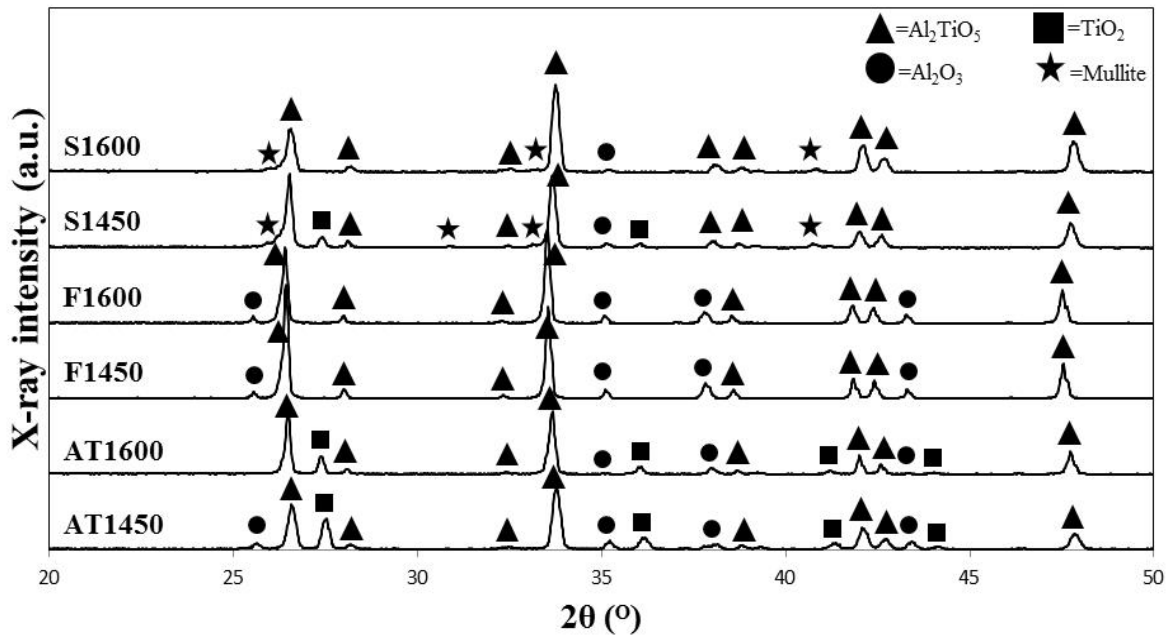


Fig. 2. XRD patterns of the sintered samples

With formation of Fe_2TiO_5 -AT solid solution, Al_2O_3 and TiO_2 become unreacted. This explains minor phases of Al_2O_3 and TiO_2 present at the XRD spectra of samples F1450 and F1600. Rezaie et al. [5] observed that additions of Fe_2O_3 decreased the formation temperature and increased the grain growth of AT. Samples with 10 wt. % SiO_2 are mainly composed of AT with small amount of mullite and trace amount of Al_2O_3 . Sample S1450 has also minor phase of TiO_2 . Mullite presence was also observed with the SEM-EDX analysis.

B. Microstructure

Figure 3 shows the general microstructure of the sintered samples. Pores and cracks are present at all samples. The samples AT1450 and AT1600 have very large cracks and pores. Abnormal grain growth is observed due to the high sintering temperatures. Also many unreacted grains are present at the microstructure. White inclusions are rutile, darker ones are corundum and the grey matrix is AT. Unreacted phases of rutile and corundum peaks are observed with XRD analysis as well. Because of the large grain size of the starting powders, with the formation of the AT, closest grains to each other are depleted and the unreacted phases are become separated. Thus, diffusion path of the ions and atoms blocked. More efficient mixing and milling could be effective to have a full formation of AT.

Samples containing 10 wt.% hematite (F1450 and F1600) have very less amount of unreacted phases. TiO_2 and Fe_2O_3 phases are not observed both with XRD and SEM analysis but unreacted Al_2O_3 is observable at the microstructure (dark grains). AT grains are abnormally grown and become more elongated.

At the microstructure of S1450, unreacted grains of Al_2O_3 and TiO_2 present and mullite ($3Al_2O_3 \cdot 2SiO_2$) is seen as dark grey color. Pores are not closed due to limited grain growth of AT. Sample S1600 includes both elongated and abnormal AT grains with grain boundary phase of mullite and glassy phase.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Special Issue 12, May 2016

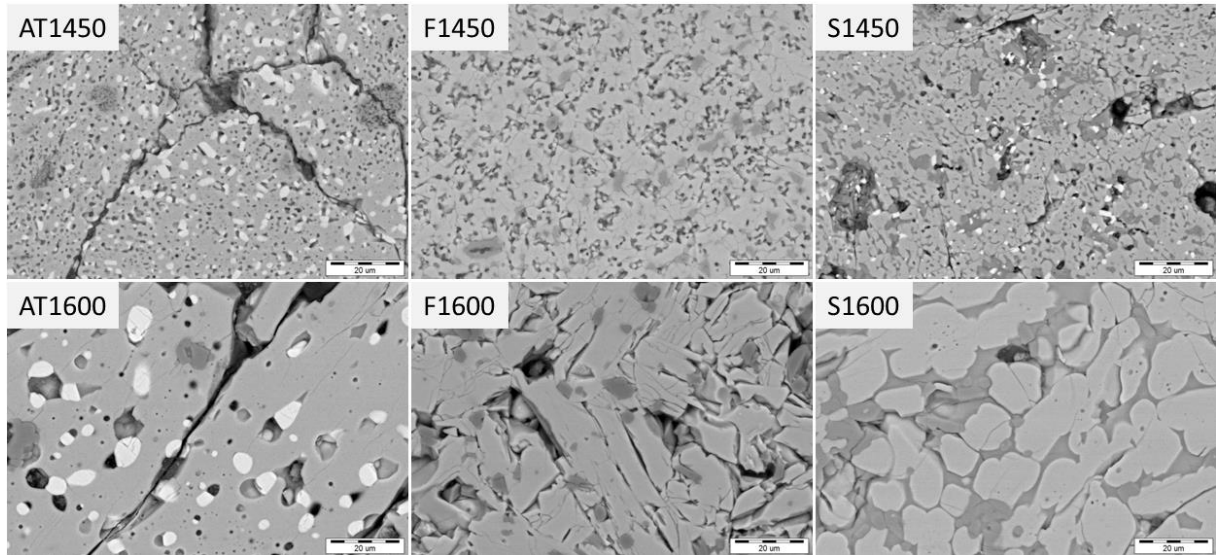


Fig.3.SEM-BSE images of the samples sintered at 1450 °C (upper) and 1600 °C (lower)

Figure 4 represents the more detailed microstructure of the sintered samples. Sample AT1450 has many unreacted grains and pores. AT-matrix is seen grey and there are no micro-cracks. Sample F1450 have unreacted Al_2O_3 grains due to the formation of Fe_2TiO_5 phase. Intergranular and transgranular micro-cracks are observed.

Unreacted grains of starting powders are present at the micro-structure of the samples S1450 and AT1600. Many cracks are present due to the thermal expansion anisotropy of the AT formation. Very large grains are formed due to the high temperature sintering of the samples. With increasing sintering temperature, grains become courser and unreacted phases decreased.

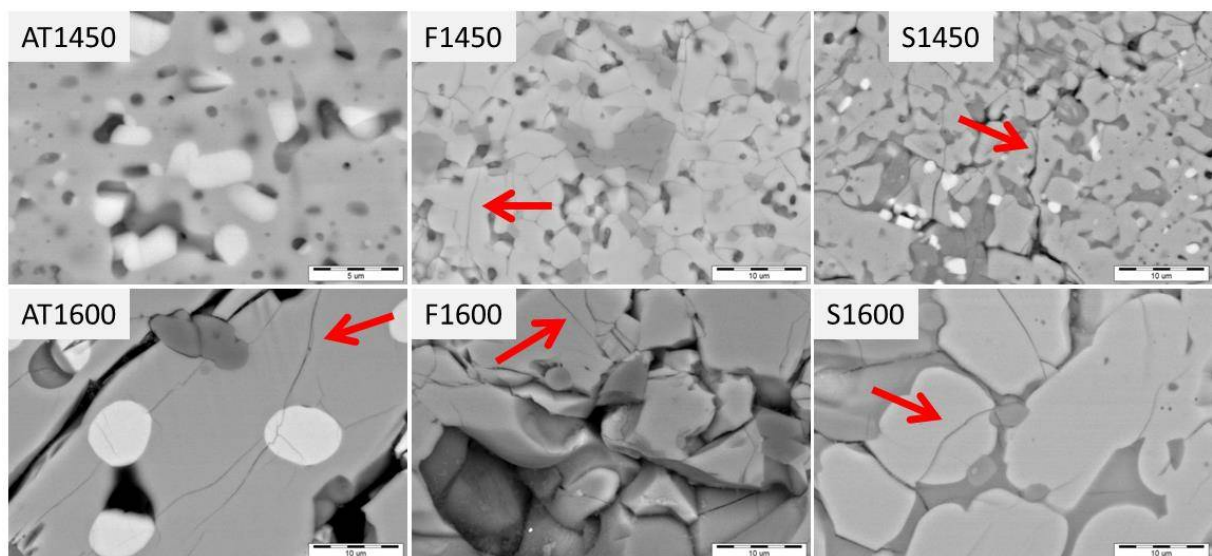


Fig.4.SEM-BSE images of the samples sintered at 1450 °C (upper) and 1600 °C (lower), arrows indicate micro-cracks

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Special Issue 12, May 2016

IV. CONCLUSIONS

Aluminum Titanate (AT) ceramics has been produced with addition 10 wt. % SiO_2 or Fe_2O_3 . Samples are sintered without and with additives at two different temperatures; 1450 and 1600°C.

Microstructure and XRD phase studies showed that unreacted Al_2O_3 and TiO_2 are remained at the samples without additives. All TiO_2 is depleted at the samples containing Fe_2O_3 due to the formation of solid solutions by diffusion of the Fe^{3+} ions to the AT crystals. Mullite and glassy phase are formed in the grain boundaries of the samples containing SiO_2 . Intergranular and transgranular micro-cracks are formed because of the high anisotropy of thermal expansion coefficients of the AT crystals during sintering or cooling. With increasing sintering temperature from 1450 to 1600°C grains become coarser and elongated.

ACKNOWLEDGMENT

The authors would like to thank Metamin A.Ş. for supporting the raw materials in this study.

This paper was presented at **icetas2016** Afyonkarahisar/Turkey.

REFERENCES

- [1] G. Bayer, "Thermal expansion characteristics and stability of pseudobrookite-type compounds, Me_3O_5 ," *Journal of the Less Common Metals*, vol. 24, no. 2, pp. 129-138, 1971.
- [2] M. Ishitsuka, T. Sato, T. Endo, and M. Shimada, "Synthesis and thermal stability of aluminum titanate solid solutions," *Journal of the American Ceramic Society*, vol. 70, no. 2, pp. 69-71, 1987.
- [3] B. Freudenberg, and A. Mocellin, "Aluminum Titanate Formation by Solid-State Reaction of Fine Al_2O_3 and TiO_2 Powders," *Journal of the American Ceramic Society*, vol. 70, no. 1, pp. 33-38, 1987.
- [4] F. J. Parker, " Al_2TiO_5 - ZrTiO_4 - ZrO_2 Composites: A New Family of Low-Thermal-Expansion Ceramics," *Journal of the American Ceramic Society*, vol. 73, no. 4, pp. 929-932, 1990.
- [5] H. Rezaie, R. Naghizadeh, N. Farrokhnia, and S. Arabi, "The effect of Fe_2O_3 addition on tialite formation," *Ceramics international*, vol. 35, no. 2, pp. 679-684, 2009.
- [6] T. Korim, "Effect of Mg^{2+} and Fe^{3+} ions on formation mechanism of aluminiumtitanate," *Ceramics International*, vol. 35, no. 4, pp. 1671-1675, 2009.
- [7] H.-C. Kim, D.-J. Lee, O.-S. Kweon, and I.-J. Kim, "Thermal Durability of Al_2TiO_5 -Mullite Composites and Its Correlation with Microstructure," *Journal of the Korean Ceramic Society*, vol. 42, no. 8, pp. 532-536, 2005.
- [8] M. Nagano, S. Nagashima, H. Maeda, and A. Kato, "Sintering behavior of Al_2TiO_5 base ceramics and their thermal properties," *Ceramics international*, vol. 25, no. 8, pp. 681-687, 1999.
- [9] I. J. Kim, and G. Cao, "Low thermal expansion behavior and thermal durability of ZrTiO_4 - Al_2TiO_5 - Fe_2O_3 ceramics between 750 and 1400 C," *Journal of the European Ceramic Society*, vol. 22, no. 14, pp. 2627-2632, 2002.
- [10] P. Oikonomou, C. Dedeloudis, C. Stournaras, and C. Ftikos, "Stabilized tialite-mullite composites with low thermal expansion and high strength for catalytic converters," *Journal of the European Ceramic Society*, vol. 27, no. 12, pp. 3475-3482, 2007.
- [11] I. Kim, and L. Gauckler, "Formation, decomposition and thermal stability of Al_2TiO_5 ceramics," *Journal of Ceramic Science and Technology*, vol. 3, no. 2, pp. 49-59, 2012.