Sintering and Mechanical Properties of Titanium Composites Reinforced Nano Sized Al_2O_3 Particles

H. Özkan Gülsoy, Semih Özbey, Serdar Pazarlioglu, Mesut Çiftci, amd Hanifi Akyurt

***Abstract*—This study aims to compare the effect of Al_2O_3 nano-particle additions on the densification, mechanical and electrochemical properties of Titanium (Ti) matrix composites. The Ti and Al_2O_3 nano-particles were dry mixed and molded using by traditional Powder Metallurgy (PM) techniques. After the molded process, the samples were sintered at 1200 ℃ and 1300 ℃ for 60 min. under high level vacuum. Mechanical property, microstructural characterization and electrochemical property of the sintered samples were performed using tensile testing, hardness, optical, scanning electron microscopy and electrochemical corrosion experiments. All the powders, fracture surfaces of sintered samples were examined using scanning electron microscope. The sintered density of straight as well as Al_2O_3 nano-particles reinforced Ti matrix composites increases with the increase in sintering time. The additions of Al_2O_3 nano-particles improve the hardness values and corrosion behavior with the increase of sintering time.**

***Index Terms*—Sintering, titanium composites, mechanical properties.**

I. Introduction

Titanium is a highly attractive material in the production of components for various applications ranging from biomedical implants to automotive fuel injectors due to its low density, high strength, good corrosion resistance and biocompatibility. At the same time, the high strength to weight ratio and high resistance to corrosion make titanium and its alloys ideal materials for many applications [1]-[3]. One major barrier to a wide spread use of titanium and titanium alloys, especially for the cost conscious industries, is the inherent high cost of materials and component fabrication. Especially, very limited consideration of Ti application in automotive industries should be noted and high cost of processing is still the major problem in this sector. Employing of powder metallurgical techniques can allow cost effective production of near-net shape components of Ti and/or Ti-base metal matrix composites. Applications and uses of titanium and titanium alloys could therefore be increased many-fold if they can be produced via PM routes at lower costs [4]-[9].

Metallic materials, alloys, ceramics, cermets and composites can be manufactured using PM technologies [8]-[11]. PM techniques would be viable solutions with lower processing cost and ease of production. As known, a metal matrix composite is constituted of a matrix material to which one or more reinforcements or fillers is added to enhance the combination of desired properties whilst minimizing the harmful effects of the material's less desirable properties [9]. Metal matrix composites have several advantages as follows [10]-[15]: high strength, high elastic modulus, high wear resistance, low sensitivity to temperature changes or thermal shock, high surface durability and low sensitivity to surface flaws, high electrical and thermal conductivity, and high vacuum environmental resistance [5]. The most prominent discontinuous reinforcements are TiC, TiN, TiCN, TiB_2, SiC, $Al_5Y_3O_{12}$, Al_2O_3 and Si_3N_4 in both whisker and particulate forms [8]-[18]. Metal matrix composites involving titanium and titanium alloys, which exhibit high wear and corrosion resistance, have also been studied [13]. Previous studies present comparisons of mechanical, wear, and corrosion behavior of metal matrix composites prepared by hot isostatic pressing (HIP) techniques using various particulate reinforcements such as Al_2O_3, TiC, TiB_2, Si_3N_4 and TiN with the corresponding unreinforced Ti matrix [11-14]. Many of the reinforcements exhibit clean interfaces free from any diffusional alloying or reactions with the Ti matrix. At the interface, TiC reinforcements were found to occur as spherical precipitates, while the TiB2 reinforcements form thick layers throughout the microstructure. The composites reinforced with some additives resulted in the least wear resistance, particularly at the higher volume fractions of the additive. The effect of particulate dispersion on the sintering behavior and mechanical properties of Ti parts were also investigated elsewhere [15]-[18]. It is reported that the composites processed with TiB_2, TiC, SiC, Si_3N_4 and TiN additions resulted in improved mechanical properties. Especially, utilizing HIP-hot isostatic pressing techniques after the shaping and sintering, leads dramatical improvements in almost all mechanical properties of the composites parts.

The present work investigates the effect of Al_2O_3 additions in nano size forms, sintering behaviour, mechanical properties and electrochemical behaviour of Ti matrix composites. Metallographic techniques were employed for the sintered tensile bars to investigate the microstructural development. Tensile and hardness properties of the sintered products were evaluated and microstructural features, powder morphology and fracture surfaces were examined under optical microscope (OM), and scanning electron microscope (SEM) techniques.

II. Experimental Procedures

In this research, the HDH Ti sponge powders (commercial purity) were provided by Phelly Materials. Al_2O_3 provided by

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Degussa AG. were used to prepare the samples. Particle size distributions for all powders were determined using Malvern Mastersizer equipment. Ti powders have particle size distribution of D_{10}: 16.05 μm, D_{50}: 32.96 μm and D_{90}: 57.15 μm. The average particle size (D_{50}) of Al_2O_3 powders were ≈10 nm. The amount of Al_2O_3 was given 1.5 wt% and 3 wt% in starting mixture and each mixture was blended in a Turbula mixer for ten hours. The mixed powders were uniaxially compacted at 600 MPa in a 80T hydraulic press with floating die. To minimize friction, compaction was carried out using zinc stearate as a die wall lubricant. The sintering response on densification and microstructures were evaluated on cylindrical pellets (12 mm diameter and 4 mm height). For measuring the tensile properties, flat tensile bars were pressed as per MPIF standard 10. Sintering of all samples was performed in a vacuum atmosphere-controlled high temperature furnace. The sintering cycle was as follows: samples were heated to 1100 ℃ at a rate of 10 ℃/min. and then the samples were heated to sintering temperatures of 1200 ℃ and 1300 ℃ at a rate of 5 ℃/min and they were held at sintering temperature for 60 min. under vacuum (10^{-5}mbar) for full densification.

The densities of the sintered samples were measured by means of the Archimedes water-immersion method. For metallographical examination, samples were cut from the center of the each sintered tensile test bar for grinding and polishing. To observe the microstructure of the sintered titanium and titanium matrix composites, Kroll's reagent (3 mL HF, 6 mL HNO_3 in 100 mL H_2O) was used to etch the samples for optical metallography (OM) examinations. All tensile tests were performed using Zwick-2010 mechanical tester at a constant crosshead speed of 1 mm/min (25 mm gauge length). The hardness tests were performed using an Instron-Wolpert Dia Testor 7551 at HRB scale. At least three specimens were tested under the same conditions to increase the reliability of the results. The fractured surfaces of the sintered samples were examined using a SEM.

III. Results and Discussion

The effect of sintering temperature and Al_2O_3 additions on the sintered density of Ti composites is shown in Fig. 1. Fig. 1 shows that at sintering temperature 1200 ℃ and 1300 ℃, pure Ti samples attained a maximum of 4.14 g/cm^3 and 4.22 g/cm^3, respectively. In 1.5 wt% and 3 wt% Al_2O_3 added samples at sintering temperature 1200 ℃ and 1300 ℃, attained a maximum density of 4.26 to 4.27 g/cm^3 and 4.25 to 4.27 g/cm^3, respectively. The densities of all samples were increased with increasing sintering temperature. However, the relative densities of all samples were not improved with increasing amount of additions. Density of 1.5 wt% Al_2O_3 addition samples were increased but, more additions level not improved density. This result shows that the more level of additions do not improve the density of samples.

Fig. 2. shows the optical micrographs of pure Ti samples with and without Al_2O_3 additions sintered at 1200 ℃ and 1300 ℃. From Fig. 2 it is evident that pure Ti sintered at 1300 ℃ has significantly lower porosity compared to the 1200 ℃ sintered samples. The increase in densification with increased temperature is accompanied by a grain growth leading to gradual closing of pores as expected. Sintering temperature increased with increasing grain size, but this increase in composite samples has remained rather limited. High level Al_2O_3 added samples present limited density than that of Ti composites at all sintering temperature, for two reasons. The first reason is the lower density of the reinforcement that reduces the density of the composite materials. The second reason is that added particles impede the sintering process.

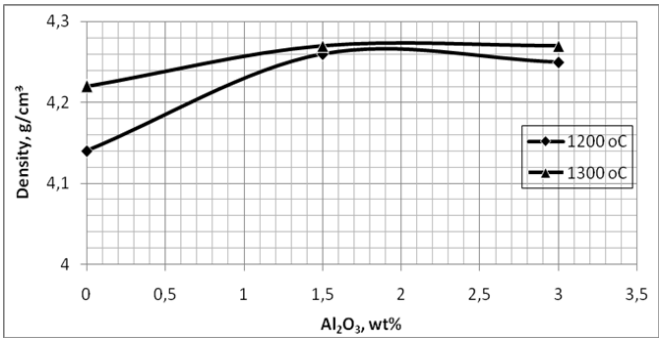

Fig. 1. Effect of sintering temperature and Al_2O_3 additions on the density of Ti composites.

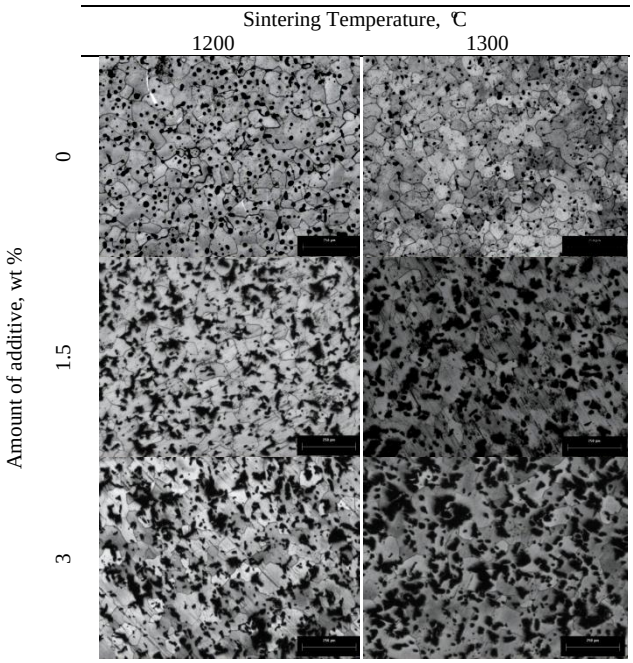

Fig. 2. Microstructure of the sintered samples.

The effect of sintering temperature and the amount of additives on tensile strength, elongation and hardness is shown in Fig. 3. Sintering temperature increases tensile strength, elongation and hardness, but all Al_2O_3 additions illustrating a considerable decrease in tensile strength and elongation. In reinforced samples, tensile strength and elongation were decreased compared with that of the base Ti samples, due to the presence of Al_2O_3 nano particles in microstructure. Literally, one may conclude that additives acted like pores throughout the microstructure leading lower percent elongation. In contrast to the effects recorded in hardness data indicate that Al_2O_3 additions cause higher hardness values and with the increment of additives (3%) hardness level is getting higher and higher. This can be rationalized in terms of the higher hardness values of Al_2O_3 particles compared to Ti particles. It is also reported that the blocking of moving dislocations by the additions also

contributes towards higher hardness levels.

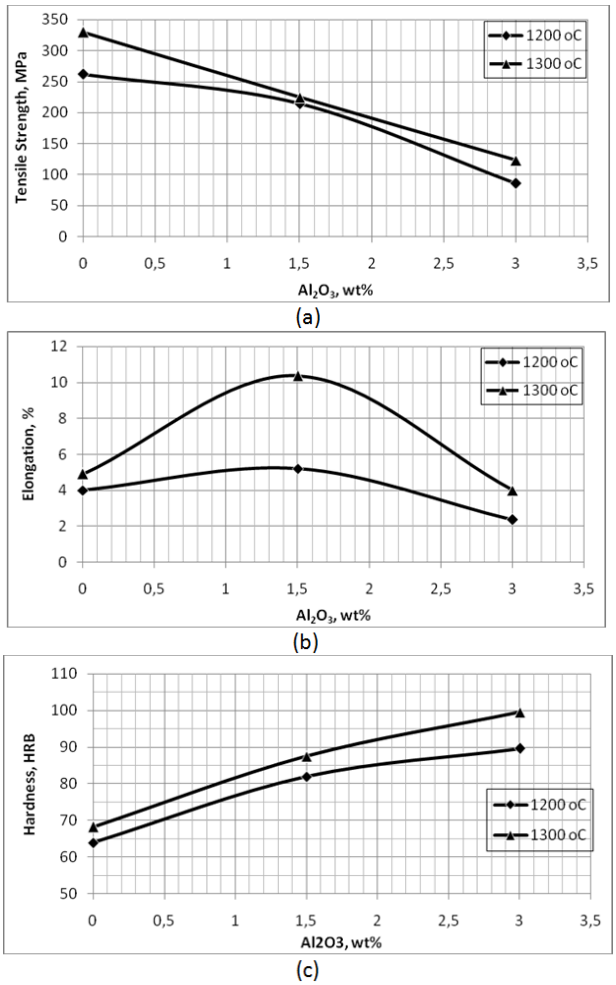

Fig. 3. Effect of Al_2O_3 additions on (a) tensile strength, (b) elongation and (c) hardness of Ti matrix composite samples.

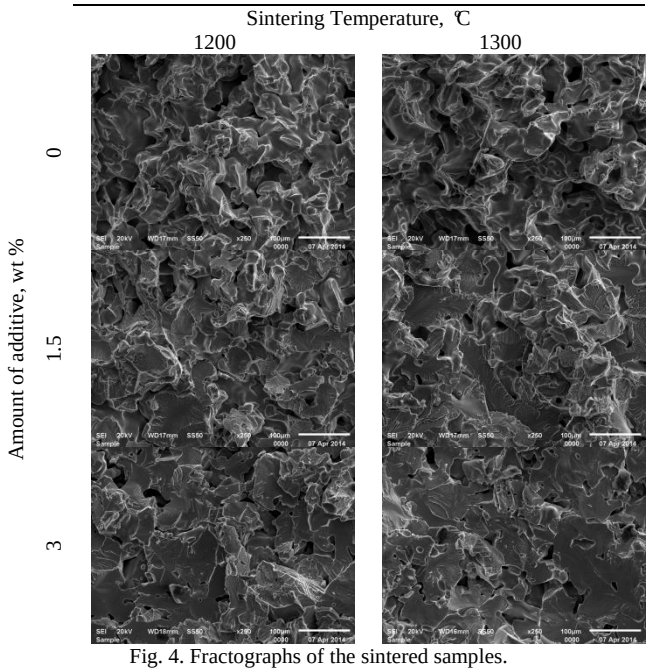

Fig. 4. Fractographs of the sintered samples.

Fig. 4 shows the fracture surfaces of Ti samples with and without additives sintered at 1200 ℃ and 1300 ℃. The samples sintered at lower temperatures still show limited densification and some particulate features throughout the microstructure are visible. For Ti samples without any additives, the main fracture mode is the separation of particles and necking areas where bonding between particles took place during sintering. In samples reinforced with Al_2O_3, the fracture mode is changed to intergranular mode due to weak grain boundary structures.

IV. Conclusion

In conclusion, experimental results show that the Ti metal matrix composite materials can be produced using PM techniques. The addition of Al_2O_3 to a titanium powder batch provided some benefit in terms of densification and hardness, but did not produce significant improvements in tensile strength and ductility. The maximum sintered density achieved in this investigation was 4.22 g/cm^3 for a Ti–3% Al_2O_3 composite. The conditions used for processing these materials lead to good adhesion between the matrix and reinforcement, allowing the improvement of some mechanical properties.

References

[1] R. M. German, *Sintering Theory and Practice*, A Wiley-Interscience Publication, USA, 1996.
[2] Y. Xu and H. Nomura, "Homogenizing analysis for sintering of bio-titanium alloy (Ti-5Al-2.5Fe) in MIM process," *J. Jpn. Soc. Powder and Powder Metall*, vol. 48, pp. 1089, 2001.
[3] R. Gerling and F. P. Schimansky, "Prospects for metal injection moulding using a gamma titanium aluminide based alloy powder," *Mater. Sci. Eng*, pp. 45, 2002.
[4] H. O. Gulsoy, V. Gunay, T. Baykara, and R. M. German, "Injection molding of mechanical alloyed Ti-Fe-Zr powder," *Mater. Trans.*, vol. 53, p. 1100, 2012.
[5] G. Adam, D. L. Zhang, J. Liang, and I. Macrae, "A novel process for lowering the cost of titanium," *Adv. Mater. Res.*, 29-30, p. 147, 2007.
[6] G. Lutjering and J. C. Williams, *Titanium*, 2nd Edition, Springer Berlin Heidelberg, New York, 2007.
[7] F. H. Froes, "Advances in titanium metal injection molding," *Pow. Metall. and Metal Ceram*, vol. 46, p. 303, 2007
[8] P. Wanjara, S. Yue, R. A. L. Drew, J. Root, and R. Donaberger, "Titanium-based composites produced by powder metallurgy," *Key Engineering Materials*, vol. 127, p. 415, 1997.
[9] F. Romero, V. Amigo, M. D. Salvador, and E. Martinez, "Mechanical and microstructural properties of titanium matrix composites reinforced by TiN particles," *Materials Science Forum*, pp. 534-536, 2007.
[10] Y. C. Li, P. D. Hodgson, and C. E. Wen, "Mechanical properties of porous Ti-26NB alloy for regenerative medicine," *Adv.in Heterog. Material Mechanics*, p. 1131, 2011.
[11] N. H. Loh, S. B. Tor, and K. A. Khor, "Production of metal matrix composite part by powder injection molding," *J. Mater. Pro. Tech*, vol. 108, p. 398, 2001.
[12] K. Morsi, V. V. Patel, S. Naraghi, and J. E. Garay, "Processing of titanium-titanium boride dual matrix composites," *J. of Mater. Proces.Techn*, vol. 196, p. 236, 2008.
[13] K. Kondoh, T. Threrujirapapong, S. Bin, H. Imai, S. F. Li, J. Umeda, and B. Fugetsu, "Multi-walled carbon nanotubes reinforced titanium composites via powder metallurgy process," *Key Engineering Materials*, vol. 520, p. 261, 2012.
[14] C. R. Anoop and P. Singh, "Ordered nanocrystalline solar cells," in *Proc. International Symposium on Research Students on Material Science and Engineering*, 2004.
[15] X. Shen, Z. Zhang, S. Wei, F. Wang, and S. Lee, "Microstructures and mechanical properties of the in situ TiB–Ti metal–matrix composites synthesized by spark plasma sintering process," *J. of Alloy. Comp*, vol. 509, p. 7692, 2011.
[16] D. E. Alman and J. A. Hawk, "The abrasive wear of sintered titanium matrix–ceramic particle reinforced composites," *Wear*, vol. 225, p. 629, 1999.
[17] H. Feng, Y. Zhou, D. Jia, and Q. Meng, "Microstructure and mechanical properties of in situ TiB reinforced titanium matrix

composites based on Ti-FeMo-B prepared by spark plasma sintering," *Compos. Sci. Technol*, vol. 64, p. 2495, 2004.
[18] V. C. Nardone, J. R. Strife, and K. M. Prewo, "Microstructurally toughened particulate-reinforced aluminum matrix composites," *Mater. Trans*, p. 171, 1991.

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