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POWDER INJECTION MOLDING OF TITANIUM MATRIX COMPOSITES[1]

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Abstract
Titanium (Ti) matrix composites based on Ti and reinforced with TiN, TiC and TiCN particles, were manufactured following a powder injection molding route: mixing, preparation of feedstock, molding, debinding and sintering. The Ti and ceramic powders were dry mixed and molded with wax based binder. The critical powder loading for injection molding was 55 vol.% for all samples. Binder debinding was performed by solvent and thermal method. After dedinding, the samples were sintered at 1,300°C for 2 hours in vacuum. Metallographic studies were conducted to extend densification and the corresponding microstructural changes. The sintered samples were characterized by measuring tensile strength, elongation and hardness. All powders and fracture surfaces of sintered samples were examined using scanning electron microscope. The sintered density of injection molded Ti and composites samples were changed with increasing amount of additions. The addition of TiN, TiC and TiCN improves the densities, tensile strength and hardness.
Key words: Powder injection molding; Sintering; Titanium.

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1 INTRODUCTION

Powder injection molding (PIM) is a manufacturing technology for the net-shape production of small, intricate, and precise metallic and ceramic parts and components. The PIM process includes mixing of powders with a binder to produce a feedstock; injection molding to form a green part with the desired shape by making the feedstock flow into and fill a mold under pressure; debinding to form a brown part by removing the binder components, and finally sintering to near full density. The process overcomes the shape limitation of traditional powder compaction, the cost of machining, the productivity limits of isostatic pressing and slip casting, and the defect and tolerance limitations of conventional casting.[1,2] If it is necessary, secondary operations such as heat and surface treatments after sintering can also be performed.[1-3]

Titanium is a highly useful material in the production of components for various applications ranging from biomedical implants to automotive fuel injectors. At the same time, the high strength to weight ratio and high resistance to corrosion make titanium and its alloys ideal materials for many of these same applications.[4-5] One major barrier to a wide spread use of titanium and titanium alloys, especially the cost conscious industry, are the inherent high cost of the materials and component fabrication. Titanium powder metallurgy (PM) approaches can allow cost effective production of near-net shape components. [6] Use of titanium and titanium alloy could therefore increase many-fold if they can be produced in the powder form at a low cost.[7,8]

Metallic materials, alloys, ceramics, cermets and composites can be manufactured using PIM technology,[4,5] but the specific applications for metal matrix composites have not been reported widely. A composite can be described as 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.[4,7] Metal matrix composites have several advantages:[3-5] high strength, high elastic modulus, 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 environment resistance.[5] The most prominent discontinuous reinforcements are TiC, TiN, TiCN, TiB, SiC, $Al_5Y_3O_{12}$, Al_2O_3 and Si_3N_4 in both whisker and particulate forms.[8-12] 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 using various particulate reinforcements such as Al_2O_3, TiC, TiB, Si_3N_4 and TiN with the corresponding unreinforced Ti matrix.[14] Many of reinforcements exhibit a clean interface free from any diffusion alloying or reactions with the Ti matrix. At the interface, TiC reinforcements were found to occur as spherical precipitates, while the TiB reinforcements formed a thick layer. The composites reinforced with some of particles resulted in the least wear resistance, particularly at the higher volume fractions. The effect of particulate dispersion on the sintering behavior and mechanical properties of Ti parts was investigated.[13-18] It is reported that the composites possessing TiB TiC, SiC, Si_3N_4 and TiN improved mechanical properties. Especially, when using the hot isostatic pressing (HIP) techniques after the shaping and sintering, all mechanical properties of the composites parts can be improved, dramatically.

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The aim of the present study is to investigate the effect of TiN, TiC and TiCN additions on the densification and mechanical properties of injection molded Ti parts for general applications. The reinforcement particles improve the theoretical densities and mechanical properties of samples with increasing amount of reinforcement particles. Thus, the injection molded titanium composites parts can be use in highly corrosive and abrasive applications such as chemical and food industries.

2 EXPERIMENTAL PROCEDURE

In this research, HDH Ti sponge powder (commercial purity) provided by Phelly Materials. The TiC, TiN and TiCN powders were obtained from H. C. Starck. Particle size distributions for all powders were determined on Malvern Mastersizer equipment. Ti powder has particle size distribution of D_{10}: 16.05 μm, D_{50}: 32.96 μm and D_{90}: 57.15 μm. Morphology of Ti powder is given in Figure 1. Ti and additive powder are irregular in shape. The average particle size D_{50} of TiC, TiN and TiCN powders were ~1-2 μm. The amount of TiC, TiN and TiCN was 1.5 wt-% and 3 wt-% in starting mixture and each mixture was blended in a Turbula mixer for 5 h.

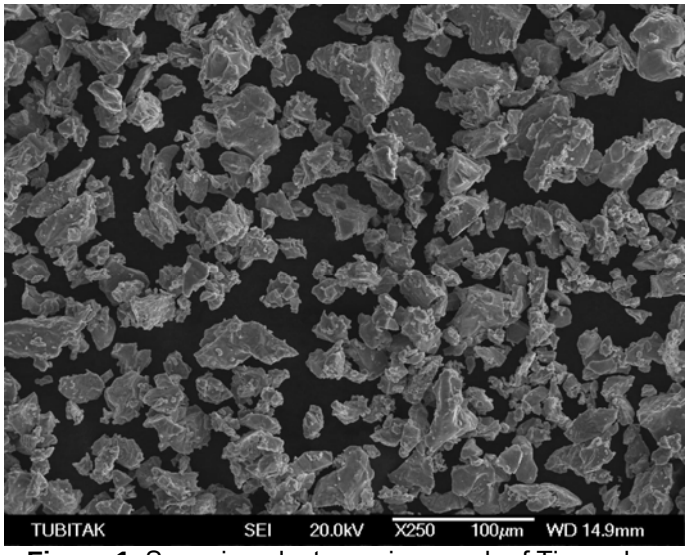

Figure 1. Scanning electron micrograph of Ti powder.

A multiple-component binder system consisting of paraffin wax (PW), polypropylene (PP), carnauba wax (CW), and stearic acid (SA) was used. Feedstock was prepared at 175ºC with the binder melted first and then powder blend added incrementally under vacuum. The powder loading in this mixture was 55 vol%. After cooling, the feedstock was pelletised by hand. These feedstocks were injected using a 12.5 MPa specially made injection-molding machine to produce tensile (MPIF 50) test specimens. The melt temperature was 150ºC, the mold temperature was kept at 35°C-40ºC and cycle time was 12 s.

Debinding was conducted in a two-step solvent/thermal operation. Green parts were solvent debinded at 70ºC for 7 h in heptanes, followed by thermal debinding step at 1ºC/min to 700ºC for 1 h in high purity Ar atmosphere. The sintering cycle applied to the samples was as follows; samples were heated to 1,300ºC sintering temperatures at a rate of 10ºC/min. and they were held at 1,300ºC for 2 hours under vacuum (10^{-5}mbar).

The densities of the sintered samples were measured by means of the Archimedes water-immersion method. For metallographic examination, samples were cut from the

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center of the each sintered tensile test bar. To observe the microstructure of the sintered titanium and titanium 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). The cross sections of sintered samples were examined using a OM. 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 guarantee the reliability of the results. The powder morphologies and fracture surfaces of the sintered samples were examined using a SEM (Jeol- JSM 6335F).

3 RESULTS and DISCUSSION

The percent theoretical density is a measurement of the residual porosity present in the composites after sintering. The theoretical density for each composite composition was determined from the theoretical densities of the starting constituents (Ti, TiC, TiN and TiCN) using the rule of the volumetric mixtures. The effect of TiC, TiN and TiCN additions on the sintered density of Ti samples is shown in Figure 2. Figure 2 shows that at a sintering temperature of 1,300ºC for 2 h, Ti samples attained a maximum theoretical density of 95.4%. 1.5% TiC, 1.5% TiN and 1.5% TiCN reinforced samples, at a sintering temperature of 1,300ºC, attained a maximum theoretical density of 97.2%, 96.4% and 95.2% respectively. For 3% additions, theoretical densities of TiC, TiN and TiCN reinforced samples attained a maximum theoretical density of 96.2%, 95.8% and 94.7% respectively. The theoretical densities of TiC and TiN reinforced samples were increased. However, TiCN caused a decrease in the theoretical density of samples. This result shows that the TiCN type additions do not improve the theoretical density of samples. The theoretical densities of all samples were decreased with increasing amount of additions. This result shows that the increasing of amount of additions do not improve the theoretical density of samples.

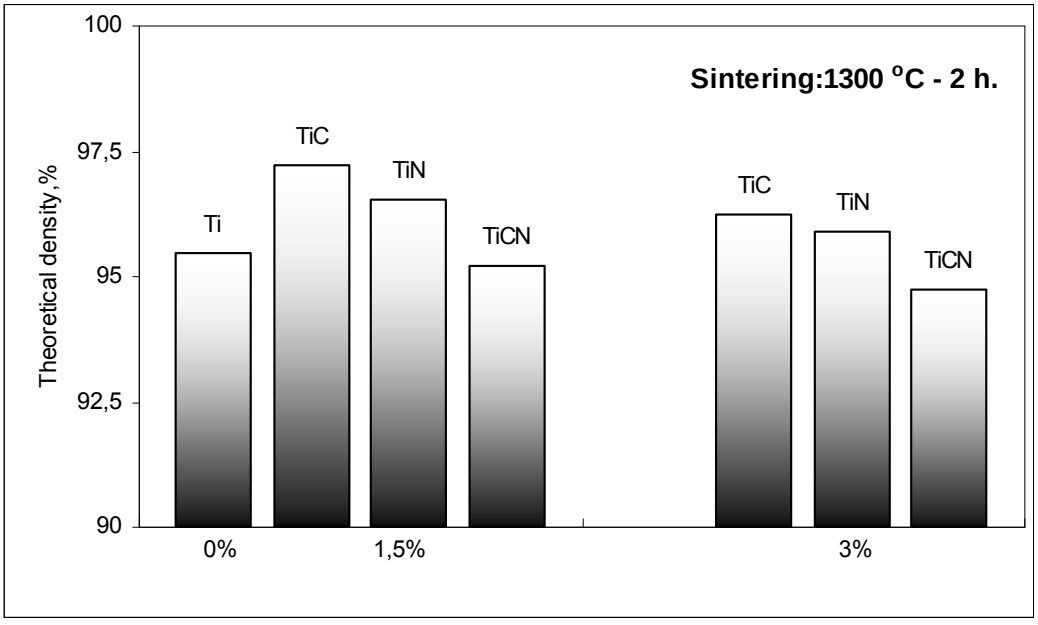

Figure 2. Effect of TiC, TiN and TiCN additions on the theoretical density of injection molded Ti samples.

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Figure 3 shows the optical micrographs of Ti samples with and without additions sintered at 1,300ºC. From Figure 3a, it is evident that Ti samples sintered at 1,300ºC have significantly porosity. This microstructure exhibits sintered particles and pores in the particles and grain boundary. Figures 3b to 3g show the microstructures of the 1.5% and 3% additions samples, respectively. With 1.5% addition, samples have low porosity and high theoretical density. But, in 3% addition samples have high porosity and low theoretical density. In composite samples, increased porosity was increased due to the increased amount of TiC, TiN and TiCN particles. The microstructure of the all Ti composites was very similar.

The effect of amount of additions of TiC, TiN and TiCN on the tensile strength (Figure 4a) and elongation (Figure 4b) of Ti sample is shown in Figure 4. The Ti sample with TiC additions shows an increase in tensile strength. But, TiN and TiCN additions decrease tensile strength. Especially, TiCN additions dramatically decrease tensile strength. In reinforced samples, elongation was decreased compared with that of base samples, due to the presence of TiC, TiN and TiCN particles in microstructure. Literally, addition particles effect on elongation as like a pore.

The effect of amount of additions of TiC, TiN and TiCN on the hardness of Ti sample is shown in Figure 5. The Ti sample with TiC, TiN and TiCN additions also shows an increase in hardness. Especially, increasing of hardness is very dramatically in TiC additions samples. This can be rationalized in terms of the enhanced hardness in Ti-TiC-TiN and TiCN composites. The additions remain segregated at grain boundaries, thereby restricting the grain growth, which further contributes towards the enhancement of the hardness. Another reason for the increase in hardness can be attributed to the inherent hardness of particles. It is also reported that the blocking of moving dislocations by the additions also contributes towards hardness. When TiC added samples are compared to TiN and TiCN added samples, the TiC added samples have higher hardness than TiN and TiCN added samples. The cause of obtained high hardness values is the presence of TiC and high theoretical density of samples.

Figure 6 shows the fracture surfaces of Ti samples with and without additions sintered at 1,300ºC. The samples sintered at lower temperatures still show particulate features. At Ti samples, main fracture mode is the separation of particles and necking areas where bonding between particles took place during sintering. In reinforced samples, the fracture mode is changed from dimpled to intergranular mode, thereby resulting in lowering of ductility. The Ti sample gives the ductility, while the reinforcement gives brittleness.

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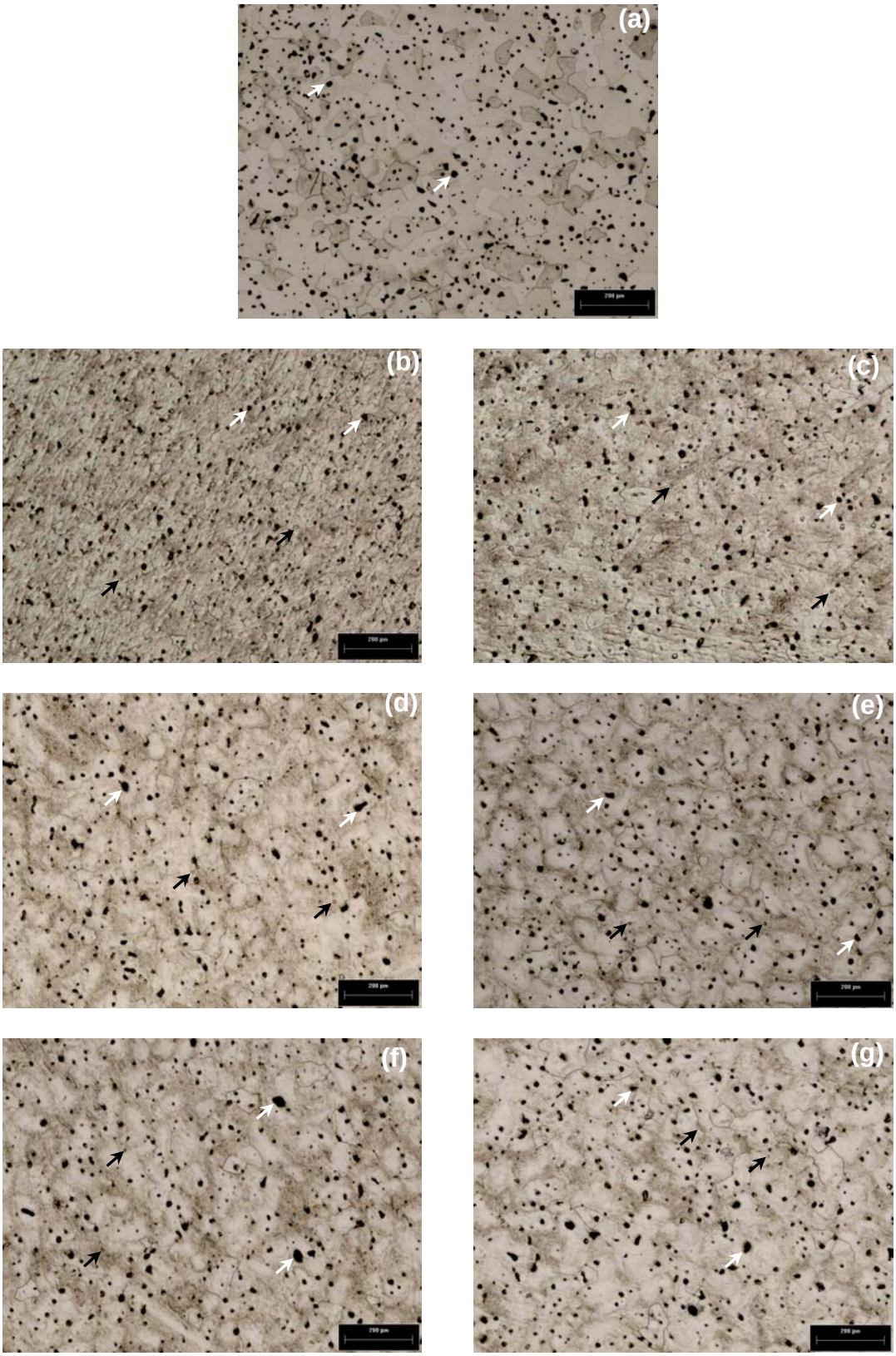

Figure 3. Microstructure of the sintered: (a) Ti; (b) 1.5% TiC; (c) 3% TiC; (d) 1.5% TiN; (e) 3% TiN; (f) 1.5% TiCN; and (g) 3% TiCN composites (white arrows indicate porosity and black arrows indicate additive particles).

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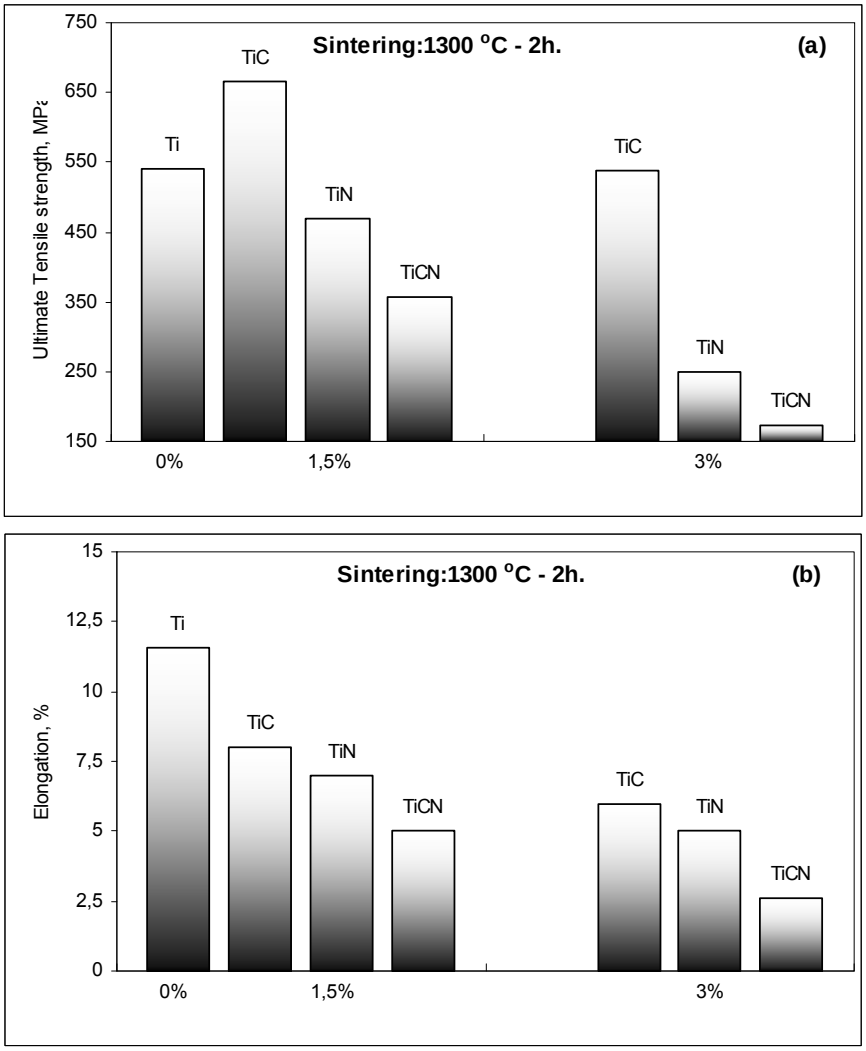

Figure 4. Effect of TiC, TiN and TiCN addition on tensile strength and elongation of injection molded Ti samples.

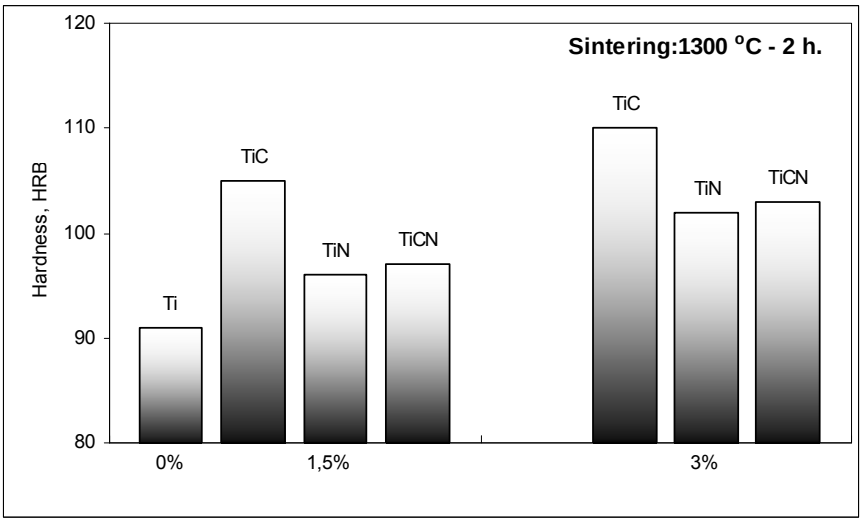

Figure 5. Effect of TiC, TiN and TiCN addition on hardness of injection molded Ti samples.

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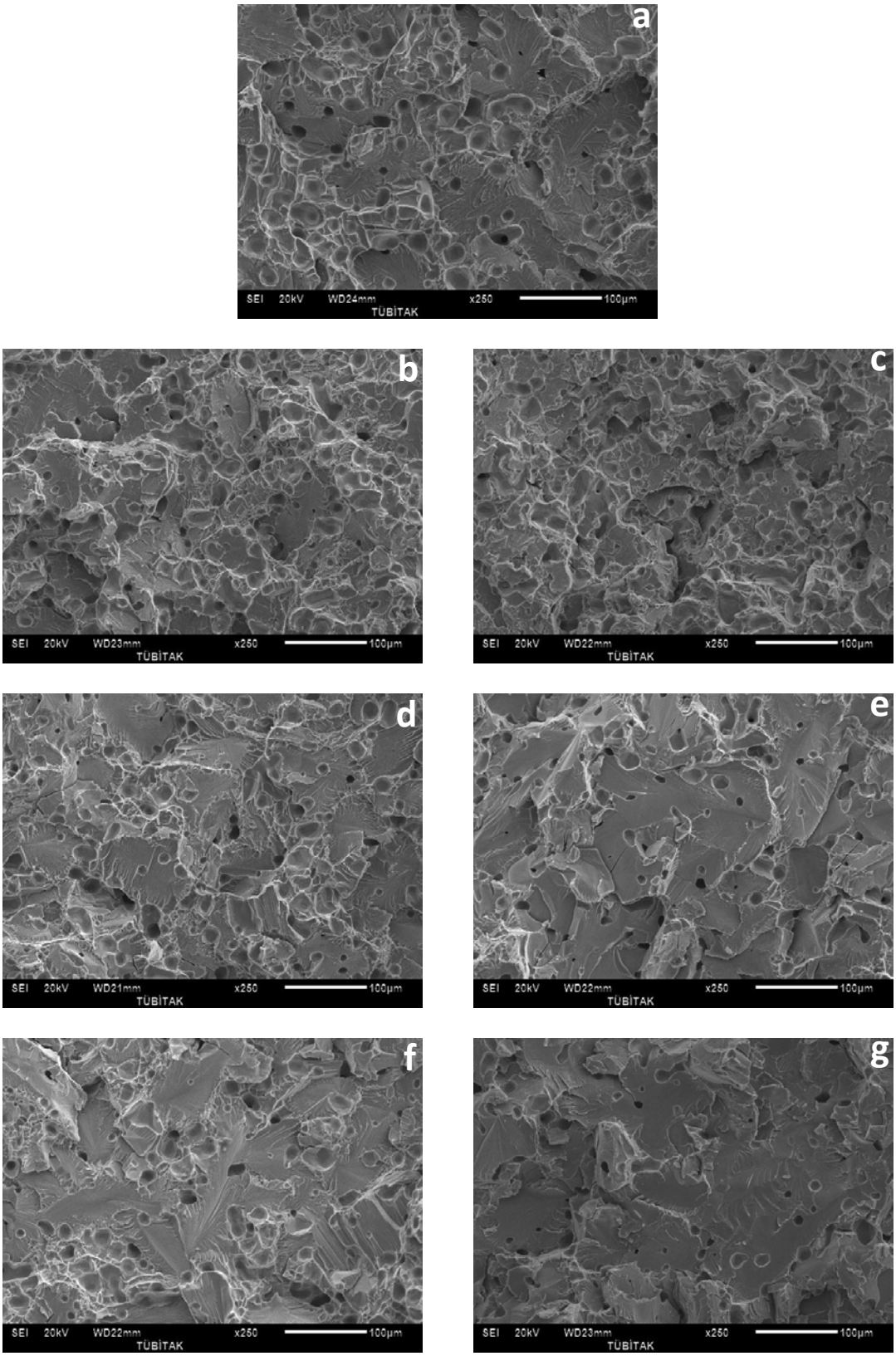

Figure 6. Fractographs (SEM) of the sintered: (a) Ti; (b) 1.5% TiC; (c) 3% TiC; (d) 1.5% TiN; (e) 3% TiN; (f) 1.5% TiCN; and (g) 3% TiCN composites.

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4 CONCLUSIONS

Experimental results show that the Ti composite materials can be produced by PIM. The addition of TiC, TiN and TiCN to a titanium powder provided some benefit in terms of sintering densification, strength and hardness, but did not produce significant improvements in ductility. The maximum sintered density achieved this study was 97.2% for a Ti-1.5% TiC composite. Tensile strength of 665 MPa and hardness of 105 HRB were achieved for Ti containing 1.5 wt% TiC. The conditions used for manufacturing these materials lead to good adhesion between the matrix and reinforcement, allowing the improvement of the properties.

Acknowledgements

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