



# Düzce University Journal of Science & Technology

Research Article

## Fabricating Graphene-Titanium (<30µm) Composites by Powder Metallurgy Method: Microstructure and Mechanical Properties

Tuğba MUTUK<sup>a,\*</sup>, Mevlüt GÜRBÜZ<sup>b</sup>

<sup>a</sup> Department of Metallurgical and Materials Engineering, Ondokuz Mayıs University, Samsun, TURKEY

<sup>b</sup> Department of Mechanical Engineering, Ondokuz Mayıs University, Samsun, TURKEY

\* Corresponding author's e-mail address: tugba.isitan@omu.edu.tr

### ABSTRACT

Titanium has extraordinary features of any metallic element such as corrosion resistance, strength to density ratio etc. Due to its good features titanium can be used in the composite as a matrix material. Titanium matrix composites (TiMCs) can be used in various industries such as automotive, airplanes and especially biomaterials. Today, as carbon reinforcing material carbon nanotube (CNT), graphite and graphene are used as reinforcing materials. The graphene has the most remarkable properties in this reinforced material due to its extraordinary mechanical features, low friction and high abrasion resistance. Composite materials produced by using titanium and graphene may have remarkable mechanical and microstructural properties. This is conspicuous subject in recent years. In the present study, graphene (Gr) reinforced titanium composites were produced by powder metallurgy method. The effect of various percentages of graphene (0-0,15-0,30-0,45-0,60 wt.%) on the microstructure, density, hardness and compressive strength of Ti composites have been investigated. From the mechanical tests after sintering at 1100°C for 120min. The highest hardness and the greatest compressive strength were obtained for 0,30 wt.% Gr reinforced composites (520.2 HV and 1137 MPa) when compared to pure titanium (419.8 HV and 780 MPa). The crystal phase and microstructure of the composites were detected by scanning electron microscopy (SEM) and X-ray diffractometer (XRD). Better mechanical properties were observed for Ti-Gr composite materials when compared pure Ti. These kinds of composites promise the future for using especially the field of biomaterials.

**Keywords:** Titanium, graphene, powder metallurgy, composite, microstructure

## Grafen-Titanyum (<30µm) Kompozitlerin Toz Metalurjisi Yöntemiyle Üretilmesi: Mikroyapı ve Mekanik Özellikler

### ÖZET

Titanyum, metalin en kullanışlı özelliklerine sahip olup, korozyon direnci ve mukavemet-yoğunluk oranı diğer metalik elementlere göre yüksektir. Alaşımız durumda, titanyum bazı çelikler kadar güçlü ama daha az yoğundur. Bu gibi özellikleri nedeniyle titanyum kompozit malzeme içinde matris malzemesi olarak

kullanılabilir. Titanyum matrisli kompozitler (TMK'ler) otomotiv, uçak endüstrileri ve özellikle biyomalzemeler gibi çeşitli endüstrilerde kullanılabilir. Bugün karbon takviye malzemesi olarak karbon nanotüp (KNT), grafit ve grafen takviye malzemesi olarak kullanılmaktadır. Grafen, olağanüstü mekanik özellikleri, düşük sürtünme ve yüksek aşınma direnci nedeniyle bu takviyeli malzemeleri içinde en dikkat çekici özelliklere sahiptir. Titanyum ve grafen kullanılarak üretilen kompozit malzemeler, dikkate değer mekanik ve mikroyapısal özelliklere sahip olabilir. Bu son yıllarda göze çarpan konulardan biridir. Bu çalışmada grafen katkılı titanyum kompozit malzemeler toz metalürjisi yöntemiyle üretilmiştir. Farklı oranlarda (%ağ. 0-0,15-0,30-0,45-0,60) katkılanmış olan grafenin titanyum kompozitin yoğunluğunda, sertliğinde, basma dayanımında ve mikroyapısında meydana getirdiği etkileri incelenmiştir. 1100°C ve 120dk. sinterleme süresinden sonra en yüksek sertlik ve basma dayanımı değerleri (520,2 HV ve 1137 MPa) saf titanyum ile karşılaştırıldığında (419,8 HV ve 780 MPa) %ağ. 0.30 grafen katkılanmış kompozit numunede elde edilmiştir. Kompozitlerin kristal fazı ve mikroyapıları taramalı elektron mikroskobu (SEM) ve X-ışını difraktometresi (XRD) ile tespit edilmiştir. Ti-Gr kompozit malzemelerin saf titanyumdan daha iyi mekanik özellikler gösterdiği gözlenmiştir. Bu tür kompozitler, özellikle biyomalzeme alanlarını kullanmak için gelecek vaat etmektedir.

*Anahtar Kelimeler: Titanyum, grafen, toz metalürjisi, kompozit, Mikroyapı*

## I. INTRODUCTION

**M**onolithic materials have limitation in achieving good combination of strength, stiffness, toughness and density. New materials need to respond to the need of technology. Therefore, metal matrix composites (MMCs) meet this demand with their superb features. The composite material is a new and combined with two or more components that are practically insoluble in one another, assembled in order to produce the material having the desired properties. A variety of composite materials is metal matrix composites. Metal matrix composites are made by adding a reinforcing material into a metal matrix. The matrix transfers the load to the reinforcement phase. Generally, lighter materials can choose as a matrix materials such as aluminium, magnesium or titanium. Titanium (Ti) can be used in lots of industry applications such as aerospace, automotive, defense and biometaterials industries. The most prominent features of Ti and Ti alloys are high biocompatibility and elastic modulus which are close to the characteristics of bone. These properties are the reasons for biomedical applications. Ti has  $\alpha$  hexagonal form at room temperature but as the temperature increases (882<sup>0</sup>C), crystal structure of Ti changes into a body-centered cubic lattice  $\beta$  form. This phase transition can make changes in microstructure and mechanical properties. [1-3].

Titanium metal matrix composites (TiMMCs) have a wide range of applications in the biomedical, automotive, and aerospace industries. TiMMCs can be added with different ceramics such as SiC, Si<sub>3</sub>N<sub>4</sub> etc. Recently, carbon-based reinforcing materials are mostly used carbon black, graphite carbon nanotubes and graphene in titanium based composite. Graphene-added materials are the most interesting subjects of recent years. Although the graphene was synthesized in 2004, composite studies on graphene have begun to increase after 2008 [4-5]. Graphene has superior thermal, electrical and mechanical properties so it has potential applications area in nano and composite technology. Graphene have been widely used as a reinforcing component in polymeric, ceramic and metallic matrices, and enhances the properties of the composite such as electrical, thermal properties and tribological treatment. However, graphene reinforced titanium studies on mechanical properties are very restricted in literature [6-10]. If we give a few studies from the literature, Cao et al studied that

the graphene nanoflake (GNF) which was added to bulk Ti matrix. GNF was added 0.5wt% in the composite. During sintering process, after specific sintering temperature (970°C) TiC was started to exist in the composite structure. This second phase (TiC) improved the mechanical properties of Ti/GNF) composite [11]. Song et al. investigated that the pure Ti was reinforced with multilayer graphene (MLG). Spark plazma sintering process was used in powder metallurgy method. The hardness values of the samples increased compared to the pure Ti. But the maximum increase was obtained 0.5wt.% MLG added composite [12].

In the present work, graphene nano platelets (GNPs) for different ratios are added to the pure titanium matrix by powder metallurgy method. The purpose of the study is to investigate and compare possible effect of pure Ti and GNPs addition on the hardness, compressive strength, and microstructure of titanium composites.

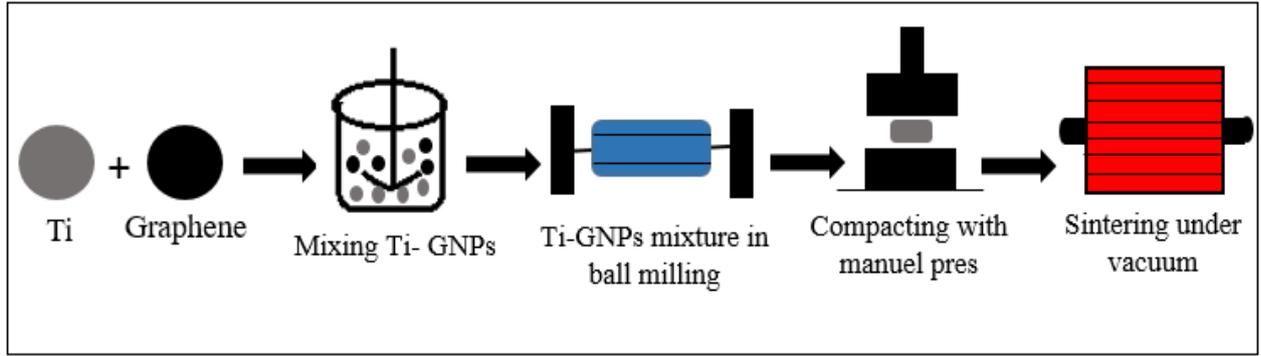
## II. MATERIALS AND METHOD

In this work, commercial Ti powder was used as a matrix material with a purity of 99.8%. Graphene nanoplatelets (GNPs) (Grafen Chemical Industries Co.) was used as a reinforced material. Powders properties are given in Table 1.

*Table 1. Properties of starting powders*

| Material | Particle Properties  | Theoretical density<br>(g/cm <sup>3</sup> ) |
|----------|--|---|
| Ti       | <30µm  | 4.5   |
| GNPs     | 5-8 nm thickness<br>5-10 µm diameter<br>120-150 m <sup>2</sup> /g (surface area) | 2.25  |

GNPs additions of 0.15, 0.30 wt%, 0.45wt% and 0.6wt% were mixed with pure Ti powder. As given in Figure 1, Ti-GNPs composites were fabricated by powder metallurgy (PM). In this method, firstly, powders were mixed with ultrasonic homogenizator, then mixed powders grinded in ball milling at 18 hours. In other step, powders were compacted with manuel press under a load of 900MPa. Then samples were sintered under vacuum in the tube furnace. The samples were heated to 1100<sup>0</sup>C for 120 min under vacuum and inert atmosphere.



*Figure 1. Schematic diagram of Ti-Gr composites fabrication using PM method*

In last step, mechanical and microstructure analyzes were done to composite materials. Micro Vickers hardness test and compressive strength test were done for mechanical analysis. Scanning electron microscope (SEM) and energy dispersive spectrometer (EDX) were used to observe microstructure and mapping analyses of the samples. Micro vickers hardness tester was used under a load of 500 g-f (HV 0.5). The measurements were performed six times and averaged value was obtained for all sintered samples with different parts on the materials surface. From the hardness trace in Fig. 2b, the hardness was calculated using Eq.(1)

$$H_v = 1.854 \frac{W}{d^2} \quad (1)$$

Where w is the applied load and d is the mean value of the diagonal length.

### III. RESULT AND DISCUSSION

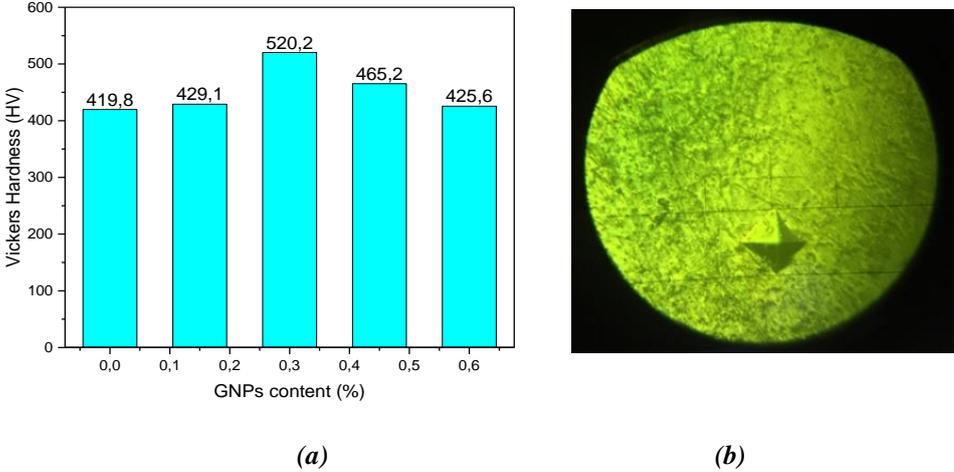
After Ti-GNPs composites powder fabrication, this powders were shaped in disc and square form. Then, they were sintered at 1100°C for 120min. to perform mechanical and microstructure analysis. Disc shaped composite samples and square samples were polished for micro Vickers hardness test and compressive strength measurement.

As present in Figure 2(a). The highest hardness was obtained for 0,30 wt.% Gr reinforced composites (520.2 HV) when compared to pure titanium (419.8 HV). The Gr reinforcement above above 0.30 wt.% reduces hardness because of nano-graphene agglomeration tendency.

The main mechanism, especially for high hardness results, is dislocation strengthening (dislocation density). Dislocation can improve Ti composites' strength due to increasing dislocation density when reinforcement size decreased. In our study, dislocation density increase because of nanosized GNPs shape. As given in Eq. (2), Vickers hardness (H) is directly proportional to the square root of dislocation density [13]

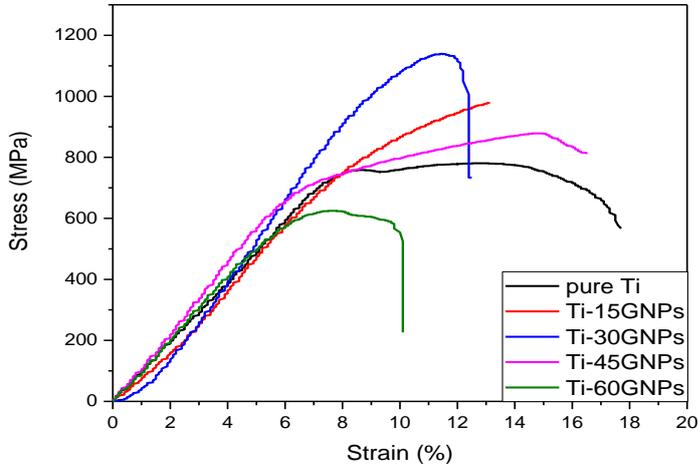
$$H = H^* + \alpha Gb\sqrt{\rho} \quad (2)$$

Where  $\rho$  is the dislocation density,  $G$  is the shear module,  $b$  is Burger's vector of dislocation,  $H^*$  and  $\alpha$  are the constants of the material.



**Figure 2.** (a) Vickers hardness test results of the Ti-GNPs composites for varying GNPs ratios (b) image from the vickers hardness tester

The greatest compressive strength were obtained for 0,30 wt.% graphene reinforced composites 1137 MPa when compared to pure titanium 780 MPa (Figure 3.). It could be explained that, GNPs located between Ti grain boundaries. The homogenous dispersion of nanosized GNPs particles prevent grain growth of Ti matrix after sintering. Grain growth can take place after sintering process and, also it causes undesired second phase in the matrix. In our sintering systems, more fine-grained composite material and more grain boundaries were obtained. The grain boundaries prevent dislocation movement during plastic deformation so the strength of the fine grain materials are increased with respect to the coarse grain materials. There are also such studies in the literature. Liu et al. [14] was studied that graphene nanosheets (GNSs)/TiC composite was produced by spark plazma sintering. GNSs from completely prevent TiC grain growth. After that, the flexural strength of GNSs/TiC composites is significantly improved. Mu et al. investigated that the graphene nanoplatelets (GNPs) in pure Ti composite. 54% higher tensile strength was obtained for 0.1wt% GNPs added composite [15].

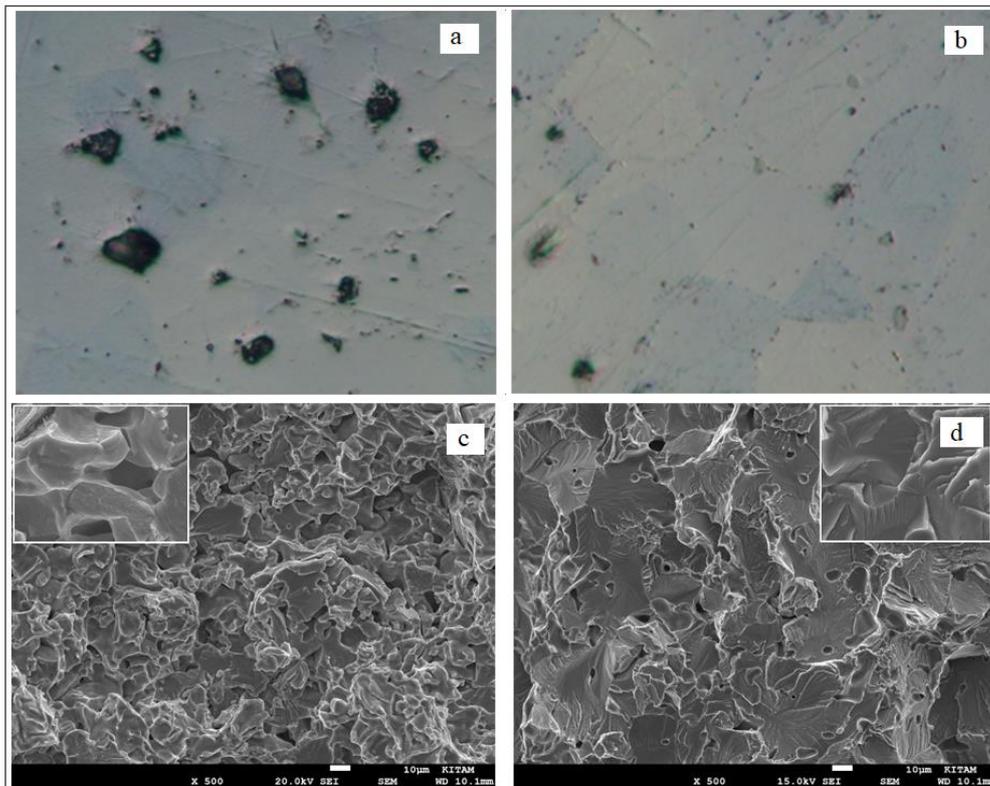


**Figure 3.** The variation of compressive strength results Ti-GNPs composites for various GNPs amount

Dislocation movement has a major role on the reinforcement of particles. When GNPs are added in the Titanium matrix, the distance between particles reduce and then the dislocation movement is tough because they face more barrier. At the same time as the distance between the particles decreases, the porous structure decreases. Thus, the improvement of composite strength can be explained by Eq. (3)[9].

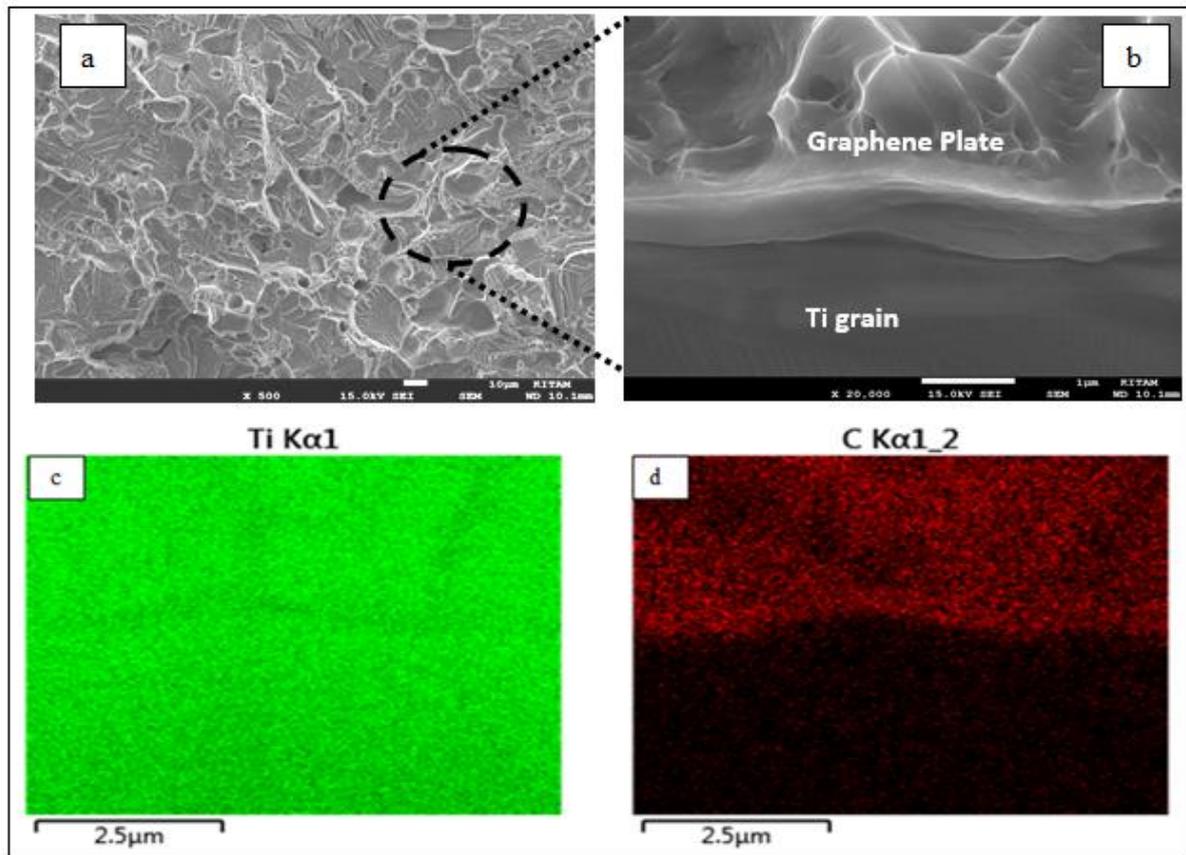
$$\sigma_c = \sigma_m f_m + \sigma_r f_r \quad (3)$$

Where  $\sigma_m$  is the strength of matrix,  $\sigma_r$  is the strength of reinforcement,  $\sigma_c$  is the strength of composite,  $f_m$  is the volume fraction of matrix,  $f_r$  is the volume fraction of reinforcement. Mechanical properties are related to microstructure and these are negatively effected by pores in microstructure. As explained in Eq.(3) when the distance between the particles reduce, the porous structure decrease in the composite. This result can be seen in stereo microscope images, where Figure 4(a-b) show pure Ti and Ti-0.30 wt% GNPs composite, respectively. Kroll's etching reagent was used on Titanium composite to obtain this stereo microscope image. As seen in Figure 4(a) more porous structure is observed in pure Titanium than Ti-GNPs composite. As given in Figure 4(c-d), it can be seen from low and high magnified SEM images that pure titanium has pore structure and 0.30 wt.% GNPs added composite has more dense microstructure which shows the best mechanical features. That is why friction among particles decrease due to solid lubricant feature of graphene. The reason for decreasing of the mechanical property with increasing amount of graphene is agglomeration tendency of graphene in nano structure. It is also due to the fact that the high-lubricating property is dominant rather than the reinforcing phase. During the plastic deformation, these agglomerations cause easy slipping between the grains and show less mechanical properties.



**Figure 4.** Stereo microscope images (50x) (a) pure Ti (b) Ti-0.30 wt% GNPs Low and high magnified SEM images (a) pure Ti (b) Ti-0.30 wt% GNPs

Microstructure and elemental analysis were studied for Ti-GNPs composite to confirm presence of graphene in structure. According to SEM images (Figure 5(a-b)), highly dense microstructure is observed, and the GNPs is located at Ti grain boundaries. As shown in EDX analyses Figure 5(c-d), elemental maps confirm the GNPs in Ti microstructure. The carbon-rich region is clearly seen in the form of plate.



**Figure 5.** (a-b) SEM images of Ti-0.30 wt% GNPs composites Low and High magnification at 1100 °C for 120 min. (c-d) and elemental maps

#### IV. CONCLUSION

GNPs-reinforced Ti (particle size of <math><30 \mu\text{m}</math>) composites were successfully manufactured by PM method. Effects of the GNPs addition on compressive strength, hardness and microstructure of Ti composites were investigated. The greatest hardness (520.2 HV) and compressive strength (1137MPa) were performed at 1100°C for 120 min. for the convenient amount of GNPs (0.30 wt.%). When compared to pure titanium (419.8 HV and 780 MPa), the graphene has a major effect on composite mechanical properties. After sintering process, highly dense and well necking between particles were obtained due to the strong graphene-titanium interphases. SEM analyses demonstrated that strong bonding and good neck formation among the particles were observed for 0.30wt% GNPs. Also, SEM and EDX analyses were confirmed the presence of graphene at grain boundary. These kinds of composites can be good candidate for biomaterials applications.

**ACKNOWLEDGEMENTS:** The authors pleased to acknowledge the financial support for this study from The Scientific and Technological Research Council of Turkey (TUBITAK) (Project No: 217M154). Also, we would like to thanks Ondokuz Mayıs University, Project Department under the grants (PYO.MUH.1901.18.007).

## V. REFERENCES

- [1] H. Attara, S. Hooyar Ehtemam-Haghighia, D. Kent and M.S. Darguscha, “Recent developments and opportunities in additive manufacturing of titanium-based matrix composites: A review,” *International Journal of Machine Tools and Manufacture*, vol. 133, pp. 85–102, 2018.
- [2] D. Banerjee and J.C. Williams, “Perspectives on titanium science and technology”, *Acta Mater.* vol. 61, pp.844–879, 2013.
- [3] F. Yastımoğlu ve A. Özkan, “Tekrarlanan Yükler Altında Kompozit Malzemelerin Yapılarının İncelenmesini Amaçlayan Deney Aygıtı Tasarımı”, *Düzce Üniversitesi Bilim ve Teknoloji Dergisi*, vol. 5, pp. 56-66, 2017.
- [4] V.M. Imayev, R.A. Gaisin and R.M. Imayev, “Microstructure and mechanical properties of near a titanium alloy based composites prepared in situ by casting and subjected to multiple hot forging”, *Journal of Alloys and Compounds*, vol. 762, pp. 555-564, 2018.
- [5] C. Chunxiang, H. BaoMin, Z. Lichen and L. Shuangjin, “Titanium alloy production technology, market prospects and industry development”, *Materials & Design*, vol. 32, pp.1684-1691, 2011.
- [6] M.G. Elkhateeb and Y.C. Shin, “Molecular dynamics-based cohesive zone representation of Ti6Al4V/TiC composite interface”, *Materials and Design*, vol. 155, pp.161–169, 2018.
- [7] G. Lütjering and J.C. Williams, *Titanium*, Second Edition, Springer, pp. 367-382.
- [8] A. Nieto, A. Bisht, D. Lahiri, C. Zhang and A. Agarwal, "Graphene reinforced metal and ceramic matrix composites: a review", *International Materials Reviews*, vol. 62, pp. 241-302, 2016.
- [9] M.C. Şenel and M. Gürbüz, E. Koç, “Fabrication and characterization of synergistic Al-SiC-GNPs hybrid composites”, *Composites Part B*, vol. 154, pp.1–9, 2018.
- [10] M.Rashad, F. Pan, A.Tang, Y.Lu, M. Asif, S. Hussain, J. She, J. Gou and J. Mao, “Effect of graphene nanoplatelets (GNPs) addition on strength and ductility of magnesium-titanium alloys”, *Journal of Magnesium and Alloys*, vol. 1, pp.242-248, 2013.
- [11] Z. Cao, X. Wang, J. Li, Y. Wu, H. Zhang, J. Guo and S. Wang, “Reinforcement with graphene nanoflakes in titanium matrix composites, *Journal of Alloys and Compounds*”, vol. 696, pp.498-502, 2017.

- [12] Y. Song, Y. Chen, W.W. Liu, W.L. Li, Y.G. Wang, D. Zhao and X.B. Liu, “Microscopic mechanical properties of titanium composites containing multi-layer graphene nanofillers”, *Materials and Design*, vol. 109, pp.256–263, 2016.
- [13] M. Gürbüz and T. Mutuk, “Effect of process parameters on hardness and microstructure of graphene reinforced titanium composites”, *Journal of Composite Materials*, vol. 52, pp.543-551, 2017.
- [14] X. Liu, J. Li, X. Yu, H. Fan, Q. Wang, S. Yan, L. Wang, “Graphene nanosheet/titanium carbide composites of a fine-grained structure and improved Mechanical Properties”, *Ceramics International*, vol. 42, pp.165–172, 2016.
- [15] X.N. Mu, H.M. Zhang, H.N. Cai, Q.B. Fan, Z.H. Zhang, Y.Wu, Z.J. Fu and D.H. Yu, “Microstructure evolution and superior tensile properties of low content Graphene nanoplatelets reinforced pure Ti matrix composites.” *Materials Science and Engineering A*, vol. 687, pp.164–174, 2017.