doi:10.55385/kastamonujes.1357436 KUJES 9(2):67-72, 2023

Kastamonu University
Journal of Engineering and Sciences
e-ISSN 2667-8209
http://dergipark.gov.tr/kastamonujes

Microstructure and Hardness Properties of Ni-Si_3N_4 Composite Materials Produced by Powder Metallurgy Method

Hasaneen Houssain[a,b], Serkan Islak[c], Uğur Çalıgülü[d, *]

[a] Department of Materials Science and Engineering, Institute of Science, Kastamonu University, Kastamonu, Türkiye
[b] Department of Chemical Engineering, Faculty of Engineering, Al Muthanna University, Samawah, Iraq
[c] Department of Mechanical Engineering, Faculty of Engineering and Architecture, Kastamonu University, Kastamonu, Türkiye
[d] Department of Metallurgy and Materials Engineering, Faculty of Technology, Fırat University, Elazığ, Türkiye
***Corresponding Author:** ugurcaligulu@gmail.com

Received: **September 08, 2023** ◆ Accepted: **December 4, 2023** ◆ Published Online: **December 26, 2023**

Abstract: In this study, the effect of the amount of Si_3N_4 on the microstructure and hardness properties of nickel (Ni) matrix silicon nitride (Si_3N_4) reinforced composite materials were investigated. Si_3N_4 was added to Ni at 5%, 10% and 15% by volume. The samples were produced using cold pressing and pressureless sintering technique. The sintering temperature was 1200 °C and the sintering time was 1 hour. SEM-EDS and XRD analyzes were used for the microstructure and phase formation analysis of the composites. The densities of the composites were measured according to the Archimedean principle. To determine the effect of Si_3N_4 on hardness properties, the microhardness of the samples was measured as Vickers. It was determined from XRD analysis that Ni, β_1 (Ni_3Si) and ε-Ni_3Si_2 phases were formed in the microstructure. As the amount of Si_3N_4 increased, both the experimental densities and relative densities decreased, and the amount of pores partially increased. Due to the distribution strengthening effect of Si_3N_4 in the Ni matrix, there was an increase in the hardness values and the highest hardness was determined as 135 HV2 with the addition of 15% Si_3N_4.

Keywords: Ni, Si_3N_4, composite, microstructure, hardness

Öz: Bu çalışmada, nikel (Ni) matrisli silisyum nitrür (Si_3N_4) takviyeli kompozit malzemelerin mikroyapı ve sertlik özellikleri üzerine Si_3N_4 miktarının etkisi araştırılmıştır. Ni içerisine Si_3N_4 hacimce % 5, % 10 ve % 15 oranında ilave edilmiştir. Numuneler soğuk presleme ve basınçsız sinterleme tekniği kullanılarak üretilmiştir. Sinterleme sıcaklığı olarak 1200 °C ve sinterleme süresi olarak 1 saat seçilmiştir. Kompozitlerin mikroyapı ve faz oluşumu analizi için SEM-EDS ve XRD analizleri kullanılmıştır. Kompozitlerin yoğunlukları Arşiment prensibine göre ölçülmüştür. Si_3N_4'ün sertlik özelliklerine etkisini belirlemek için numunelerin mikrosertlikleri Vickers olarak ölçülmüştür. Mikroyapıda Ni, β1 (Ni_3Si) ve ε-Ni_3Si_2 fazlarının oluştuğu XRD analizinden tespit edilmiştir. Si_3N_4 miktarının artmasıyla hem deneysel yoğunluklarda hem de bağıl yoğunluklarda azalma meydana gelmiş olup, kısmen gözenek miktarı artmıştır. Si_3N_4'ün Ni matris içerisinde dağılım mukavemetlendirme etkisi göstermesinden dolayı sertlik değerlerinde artış olmuş ve en yüksek sertlik %15 Si_3N_4 ilavesinde 135 HV2 olarak tespit edilmiştir.

Anahtar Kelimeler: Ni, Si_3N_4, kompozit, mikroyapı, sertlik

1. Introduction

Metal matrix composites (MMCs) are an engineering combination of a continuous metallic matrix and a reinforcement, usually ceramic. While aluminum, titanium, copper, nickel, magnesium and their alloys are used as matrix, oxide, carbide, nitride and borides are used as ceramic reinforcement [1-4]. Ni-based alloys are widely used in chemical plant, nuclear power plant, oil field and some corrosive environments due to their superior corrosion resistance [5]. However, Ni has poor mechanical properties for high temperature applications. This drawback can be overcome by producing Ni matrix composites [6]. There are studies conducted by producing MMCs to improve mechanical properties. Jiang et al. [7] produced Ni matrix graphene reinforced composites by in-situ method and stated that graphene in Ni increased the strength. Islak et al. [8] by adding TiC to the Ni-based alloy powder, they produced the NiCrBSi matrix TiC reinforced composite by hot pressing technique, one of the powder metallurgy methods, and stated that the friction coefficients decreased and the hardnesses increased as the TiC ratio increased. Islak et al. in a different study [9], they produced hybrid composites by powder metallurgy method by adding carbon nanofiber (CNF) and boron carbide (B_4C) to the nickel matrix. They reported that the hardness increased by 44% and the wear rate decreased by approximately 10 times in the Ni-10B_4C-2CNF composite compared to neat Ni.

Covalently bonded silicon nitride (Si_3N_4) ceramics have been studied in recent years for shaping, sintering and microstructure control in high temperature and wear resistant applications due to their attractive combination of mechanical and thermal properties [10]. Because of its superior properties and because it has never been added to the Ni matrix in previous studies, we planned to produce Ni-Si_3N_4 composite and examine some of its properties in this study.

2. Material and Method

In this study, Ni powder with 2 µm grain size and 99.5% purity and Si_3N_4 powder with 10 µm grain size and 99.9% purity were used to produce Ni-Si_3N_4 composites. Ni powder was obtained from Nanokar Nanotechnology company, and Si_3N_4 powder was obtained from Nanografi Nanotechnology company. The powders were mixed in the turbula for 1 hour in the proportions given in Table 1, and were cold pressed in the hydraulic press at 600 MPa pressure in the form of pellets with a diameter of 20 mm and a thickness of 5 mm. Then, the pellets were sintered in a tube furnace at 1200 ºC for 1 hour in an argon atmosphere.

Table 1. Powder composition rates in composite production

Sample group	Composition (vol.%)	
	Ni	Si_3N_4
N0S	100	0
N5S	95	5
N10S	90	10
N15S	85	15

The samples were sanded using 320-2000 mesh grit sandpaper and polished with diamond solution. Then, it was etched for microstructure imaging in 100 ml distilled water + 25 ml hydrochloric acid + 8 g iron (III) chloride solution. FEI QUANTA 250 FEG brand scanning electron microscope, and X-ray diffraction (Bruker D8 Advance) analyzes were used to examine the microstructure of samples and determine phase compound. The experimental densities of the samples were measured according to the Archimedes principle, as specified in ASTM B 962 [11]. The hardness of the samples was determined using the Shimadzu HMV-G21 model microhardness device according to the ASTM E92-17 standard [12] at a load of 2 kg and a dwell time of 15 seconds. Measurements were made from 5 different points for each test and average values presented in the study.

3. Result and Discussions

SEM-EDS analysis of the pure Ni matrix is given in Figure 1. It is clearly seen from the SEM photo in Figure 1a that very little porosity occurs in the sample. Again, according to the SEM photo, it is understood that a compact structure has been formed. However, scratches formed during metallographic sample preparation are also noticeable. In the EDS analysis of the N0S sample, it is seen that the structure consists of 100% Ni and there is no oxygen in the structure. The absence of oxygen caused the Ni powder particles to bond better with each other during the sintering process.

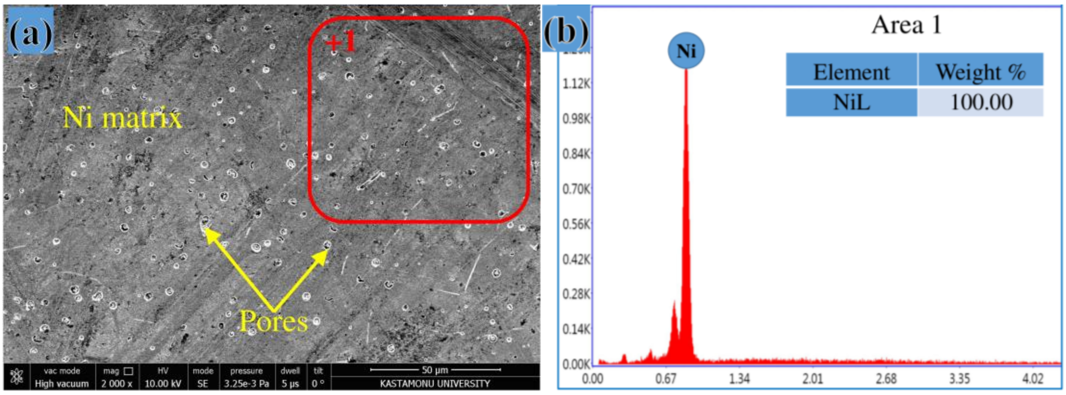

Figure 1. For the N0S (Ni) sample: (a) SEM photograph, and (b) EDS analysis

Figure 2 shows general SEM, detailed SEM and EDS analysis of Ni-15%Si_3N_4 composite. It is understood from SEM photographs that a phase transformation microstructure is formed. The reason for this may be that there is partial melting during the sintering process. It can be seen from Figure 2a that the microstructure has a dendritic morphology. ε-Ni_3Si_2 precipitates were formed between the Ni+β1-Ni_3Si phase dendritic arms (Figure 2b). It is clear from the EDS analysis of point 1 and point 2 in Figure 2c that the mentioned structures are formed. The formation of these phases is given in the XRD graph in Figure 3. When Si_3N_4 was added to Ni, the amount of Ni phase decreased and β_1-Ni_3Si and ε-Ni_3Si_2 phases became evident. Xie et al. [13] in their study, it was determined that dendritic structures were formed and the above-mentioned phases were formed. Oxidation has occurred in the dendritic arms. The presence of oxygen in the EDS analysis at point 3 also supports this. The oxide formation here may have occurred in the form of SiO_2. Shen et al. [14] reported that black mottled SiO_2 structure was formed by oxidation of silicon in their study.

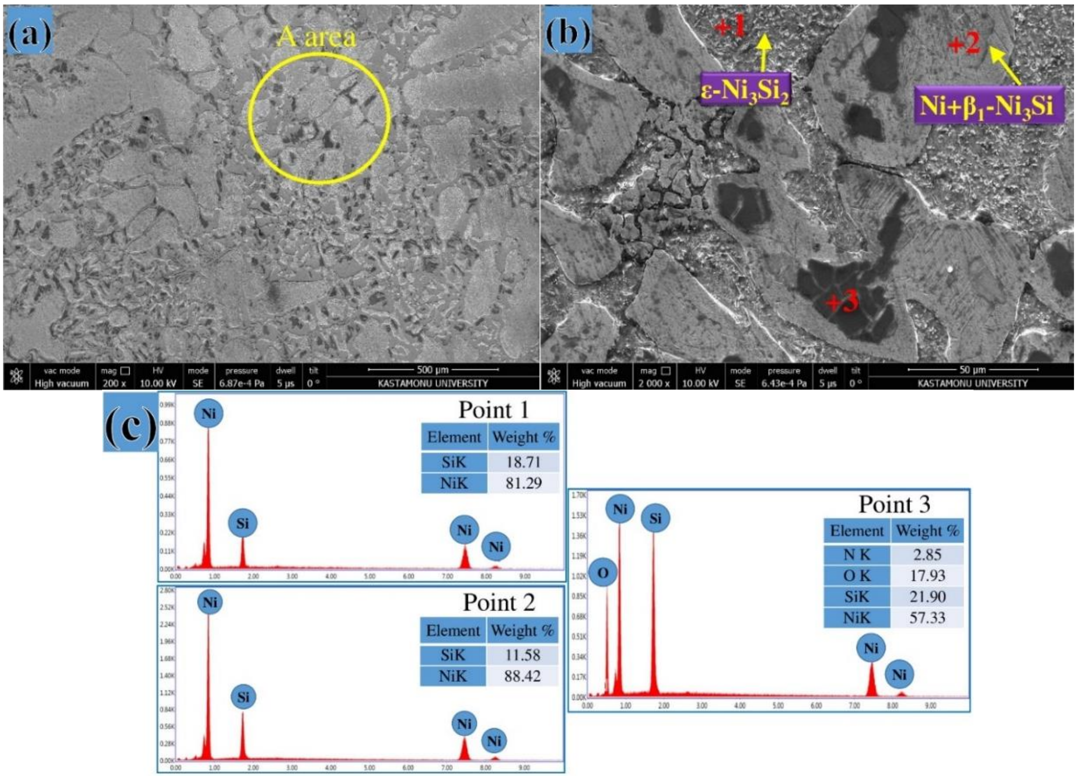

Figure 2. For the N15S (Ni-15%Si_3N_4) sample: (a) general SEM photograph, (b) detailed SEM photograph of area A, and (c) EDS analysis

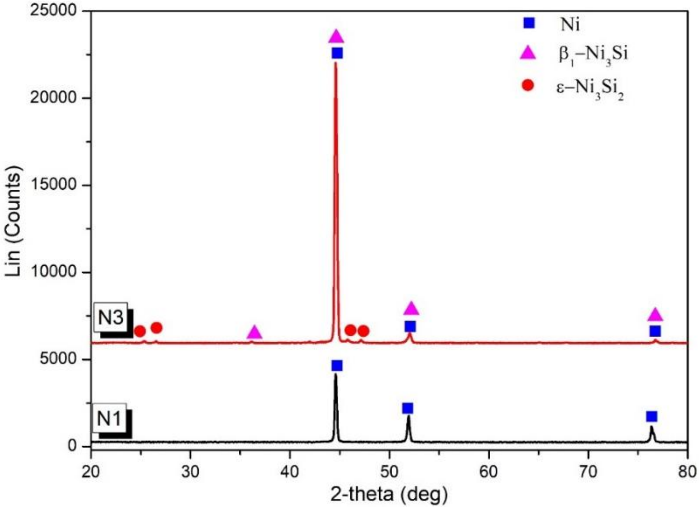

Figure 3. XRD analysis graph of N0S and N15S samples

Figure 4 gives a graph showing the effect of Si_3N_4 addition on experimental density, relative density and porosity of Ni-Si_3N_4 composites. According to the graph, experimental density and relative density decreased and porosity increased with increasing the addition of Si_3N_4. While the experimental densities for N0S, N5S, N10S and N15S were 8.64 g/cm^3, 7.95 g/cm^3, 7.55 g/cm^3 and 7.21 g/cm^3, respectively, the relative densities were calculated as 97.06%, 92.30%, 90.67% and 89.68%, respectively. The reason for the decrease in density is that the density of the reinforcing element Si_3N_4 (3.17 g/cm^3) is quite low compared to the density of the Ni matrix (8.9 g/cm^3). Islak and Çelik [15] added B_4C to bronze and produced bronze-B_4C diamond sockets and reported that the densities decreased as the amount of B_4C increased. Kriewah and Islak [16] reported that reinforcement elements with low density compared to the matrix reduce the density of the composite. The reason for the decrease in relative densities is based on two fundamentals. The first of these is that the ceramic particles added to the metallic matrix negatively affect the sinterability and prevent the matrix particles from necking. The other is the melting temperature difference between the matrix and the reinforcement elements [17]. The porosity rates were calculated as 2.94%, 7.70%, 9.33% and 10.32% for N0S, N5S, N10S and N15S, respectively. The increase in porosity can be associated with the reasons for the decrease in relative density.

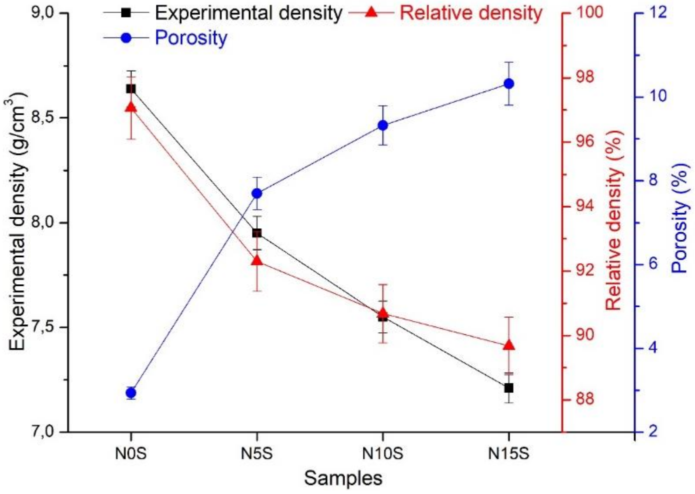

Figure 4. Experimental density, relative density, and amount of porosity of the samples.

Figure 5 shows the effect of Si_3N_4 reinforcement on hardness values, which is the most basic mechanical property determination test for Ni-Si_3N_4 composites. While the hardness value measured for the pure N0S sample is 105 HV2, the hardness values for N5S, N10S and N15S with the addition of Si_3N_4 are 110 HV2, 123 HV2 and 134 HV2, respectively. The increase in hardness is clearly seen with the addition of Si_3N_4. With the addition of 15% Si_3N_4, the hardness increase was 28% compared to the sample without additives. It can be said that this increase in hardness is caused by the distribution of the Si_3N_4 reinforcement element in the matrix [18]. In other words, the increase in hardness can be explained by the mixing rule. Mixing rule for materials with high relative density (Equation 1):

$$\boldsymbol{H_C = H_m f_m + H_r f_r} \qquad \textbf{(1)}$$

Here, H_c is the hardness of the composite, H_m is the hardness of the matrix, H_r is the hardness of the reinforcement element, and f_m and f_r are the volumetric ratio of the matrix and reinforcement element, respectively [19-21]. Buytoz et al. [22] stated that TiC particles in Cu-TiC composites produced by hot pressing technique caused higher dislocation density in the composite. This causes an increase in hardness. Additionally, ceramic particles added to composites cause an increase in strength by preventing the movement of dislocations [23, 24].

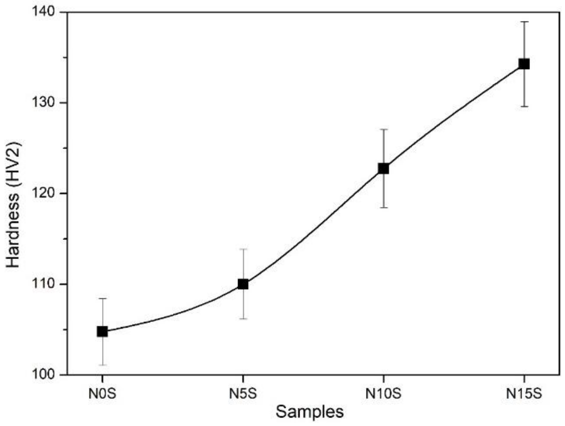

Figure 5. Hardness graph of Ni-Si_3N_4 composites

4. Conclusion

The following results were obtained in the study on the properties of Ni matrix Si_3N_4 reinforced composites produced by powder metallurgy.

A compact and less porous microstructure was obtained in the pure Ni sample. With Si_3N_4 addition, the microstructure had a dendritic morphology.

According to XRD analysis, Ni, β_1-Ni_3Si and ε-Ni_3Si_2 phases were formed in the microstructure. Ni+β_1-Ni_3Si phase was formed in the dendrite arms, and ε-Ni_3Si_2 phase was formed between the dendrite arms. The formation of these phases is also supported by EDS analysis.

With the increase of Si_3N_4 contribution, there was a decrease in experimental and relative densities, an increase in porosity, and a significant increase in hardness values. With the addition of 15% Si_3N_4, there was a 28% increase in hardness compared to the sample without additive.

Conflict of Interest

All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

Ethics Committee Approval

N/A

Author Contribution

Conceptization: HH, SI, UÇ; methodology and laboratory analyzes: HH; writing draft: HH, SI, UÇ; proof reading and editing: HH, SI, UÇ. Other: All authors have read and agreed to the published version of manuscript.

Funding

The author declared that this study has received no financial support.

5. References

[1] Kondoh, K. (2015). Titanium metal matrix composites by powder metallurgy (PM) routes. In Titanium powder metallurgy. Butterworth-Heinemann, 277-297.

[2] Samer, N., Andrieux, J., Gardiola, B., Karnatak, N., Martin, O., Kurita, H., Chaffron, L., Gourdet, S., Lay, S., & Dezellus, O. (2015). Microstructure and mechanical properties of an Al–TiC metal matrix composite obtained by reactive synthesis. Composites Part A: Applied Science and Manufacturing, 72, 50-57.

[3] Rohatgi, P. K. (1993). Metal matrix composites. Defence science journal, 43(4), 323-349.

[4] Evans, A., San Marchi, C., Mortensen, A., Evans, A., San Marchi, C., & Mortensen, A. (2003). Metal matrix composites. Springer US, 9-38.

[5] Kumar, B. A., Ananthaprasad, M. G., & Krishna, K. G. (2015). A review on corrosion behavior of nickel matrix composites. International Journal of Emerging Technology and Advanced Engineering, 5(10), 342-346.

[6] Kumar, B. A., Ananthaprasad, M. G., & GopalaKrishna, K. (2016). A review on mechanical and tribological behaviors of nickel matrix composites. Indian Journal of Science and Technology, 9(2), 1-7.

[7] Jiang, J., He, X., Du, J., Pang, X., Yang, H., & Wei, Z. (2018). In-situ fabrication of graphene-nickel matrix composites. Materials Letters, 220, 178-181.

[8] Islak, S., Ulutan, M., & Buytoz, S. (2020). Microstructure and Wear Properties of Hot-Pressed NiCrBSi/TiC Composite Materials. Russian Journal of Non-Ferrous Metals, 61(5), 571-582.

[9] Islak, S., Koç, V., & Gariba, A.M.M. (2022). Wear and microstructural properties of Ni-B_4C/CNF composites. Science of Sintering, 54(4), 439-448.

[10] Han, I. S., Seo, D. W., Kim, S. Y., Hong, K. S., Guahk, K. H., & Lee, K. S. (2008). Properties of silicon nitride for aluminum melts prepared by nitrided pressureless sintering. Journal of the European Ceramic Society, 28(5), 1057-1063.

[11] ASTM B962-08. (2008). Standard test methods for density of compacted or sintered powder metallurgy (PM) products using Archimedes' principle.

[12] ASTM E92-17. (2017). Standard test methods for Vickers hardness and Knoop hardness of metallic materials. West Conshohocken (PA): ASTM International.

[13] Xie, H., Jia, L., & Lu, Z. (2009). Microstructure and solidification behavior of Cu–Ni–Si alloys. Materials Characterization, 60(2), 114-118.

[14] Yu, L., Shen, F., Fu, T., Zhang, Y., Cui, K., Wang, J., & Zhang, X. (2021). Microstructure and oxidation behavior of metal-modified Mo-Si-B alloys: A review. Coatings, 11(10), 1256.

[15] Islak, S., & Çelik, H. (2015). Effect of sintering temperature and boron carbide content on the wear behavior of hot pressed diamond cutting segments. Science of Sintering, 47(2), 131-143.

[16] Kriewah, O. A. E., & Islak, S. (2022). Synthesis of Cu-Cr-B_4C-CNF hybrid composites. Kastamonu University Journal of Engineering and Sciences, 8(2), 90-97.

[17] Rahimian, M., Ehsani, N., Parvin, N., & reza Baharvandi, H. (2009). The effect of particle size, sintering temperature and sintering time on the properties of Al–Al_2O_3 composites, made by powder metallurgy. Journal of Materials Processing Technology, 209(14), 5387-5393.

[18] Min, K. H., Lee, B. H., Chang, S. Y., & Do Kim, Y. (2007). Mechanical properties of sintered 7xxx series AI/SiC_p composites. Materials Letters, 61(11-12), 2544-2546.

[19] Kim, H. S. (2000). On the rule of mixtures for the hardness of particle reinforced composites. Materials Science and Engineering: A, 289(1-2), 30-33.

[20] Kumar, G. V., Rao, C. P., & Selvaraj, N. (2011). Mechanical and tribological behavior of particulate reinforced aluminum metal matrix composites–a review. Journal of minerals and materials characterization and engineering, 10(01), 59-91.

[21] Okay, F., & Islak, S. (2022). Microstructure and mechanical properties of aluminium matrix boron carbide and carbon nanofiber reinforced hybrid composites. Science of Sintering, 54(2), 125-138.

[22] Buytoz, S., Dagdelen, F., Islak, S., Kok, M., Kir, D., & Ercan, E. (2014). Effect of the TiC content on microstructure and thermal properties of Cu–TiC composites prepared by powder metallurgy. Journal of Thermal Analysis and Calorimetry, 117, 1277-1283.

[23] Yang, S., Guo, Z., & Xia, M. (2018). Effect of TiB content on the properties of Al-TiB composites. Science of Sintering, 50(2), 237-244.

[24] Islak, S. (2019). Mechanical and corrosion properties of AlCu matrix hybrid composite materials. Science of Sintering, 51(1), 81-92.