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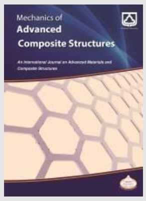

Metallurgical Assessment of Graphite Reinforced Al-Cu-Mg Nanocomposites Produced by the Shaker Mill Method

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KEYWORDS

Powder metallurgy;
Aluminum nanocomposite;
Graphite;
Shaker mill;
Sintering.

ABSTRACT

This research investigated the effects of graphite content on the sintering behavior of Al-4.5Cu-1.5Mg produced by the shaker mill method. The shaker mill method was chosen because it is able to form uniform nanoparticles in a such short time due to its very high-speed milling. Powder morphology after the shaker mill was investigated. The damaging, fracturing, and cold-welding process during the shaker mill happened in such a shorter time leading to more homogenously dispersed graphite-reinforced Al-4.5Cu-1.5Mg matrix nanocomposite. Sintering under high-purity argon gas for 99.999% was carried out to produce high-density material from 550°C to 620°C. Sintering properties showed that graphite content for more than 0.5wt% decreased sintering density which leads to a lower hardness value. Based on microstructures, a higher amount of graphite is prone to have bigger porosity due to its agglomeration which leads to produced voids between grains. Agglomeration of graphite is still the main challenge for the manufacturing of graphite-reinforced metal matrix nanocomposites. Aluminum carbide Al_4C_3 was found and it was expected as a result of a reaction between Al and graphite during very high-speed milling. Aluminum carbide acts as an interface between matrix and reinforcement when in certain conditions is able to transfer load from matrix to reinforcement particles leading to improved mechanical properties. Intermetallics of Al-Cu and Al-Mg were also found after sintering.

1. Introduction

Nanocomposites refer to materials that consist of a nanocrystalline structure of small nanocrystals incorporated within or between the nanoscale matrix grains [1]. Nanoscale second-phase particles such as borides, carbides, nitrides, oxides, and hydrides are commonly incorporated in these nanocomposites [2]. Nanocomposite materials are usually classified on the basis of the physical or chemical nature of the matrix phase, e.g., polymer matrix, metal-matrix, and ceramic nanocomposites [3,4].

Aluminum matrix nanocomposites are widely used because of their excellent combination of properties [5,6]. Applications of such materials take place in automobile, aerospace, defense, and other related sectors. In the automobile sector, aluminum composites are used to produce various components such as brake drums, cylinder liners, cylinder blocks, and driveshafts [7,8]. Among the various matrix materials available, aluminum and its alloys are widely used in the fabrication of metal matrix nanocomposites and have reached the industrial production stage. The emphasis has been given to developing affordable aluminum-based metal matrix nanocomposites with various hard and soft reinforcements (SiC, Al_2O_3, graphite, and mica) because of the likely possibilities of these combinations informing highly desirable composites.

There are many ways to prepare these nanocomposites, among which an economical way of producing metal matrix nanocomposites is mechanical alloying [1]. In the 1960s mechanical alloying (MA) technique was used for the production of an oxidation-resistant alloy. Mechanical alloying (MA) is a powder processing technique that allows the production of

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homogeneous materials starting from blended elemental powder mixtures [9,10]. The MA is a unique process in that a solid-state reaction takes place between the fresh powder surfaces of the reactant materials at room temperature [11]. Consequently, it can be used to produce alloys and compounds which are difficult or impossible to be obtained by the conventional melting and casting technique [12].

At atmospheric pressure, graphite is more stable form of carbon, because of the very stable bonds between the atoms, graphite is very difficult to bond with another element [13-15]. Many researchers have been investigating the manufacturing process of carbon-based materials reinforced aluminum matrix nanocomposites. CNT, graphene, graphite, and diamond have been used as reinforcements to produce aluminum metal matrix nanocomposites. Agglomeration due to its strong affinity between particles has been a challenge to manufacture nanocomposites [16-18]. High energy ball mill is commonly used to produce graphite-reinforced aluminum matrix nanocomposites. But it leads to some unnecessary disadvantages such as manufacturing time.

The shaker mill technique is able to produce homogenous nanoparticles in such a short time because of the continuous process of fracturing and welding of powder by ball mill at high speed. Agglomeration of graphite or any other carbon-based reinforcement materials is the main challenge in manufacturing this kind of nanocomposites due to its very high stability. The Shaker mill technique is expected to successfully produce graphite-reinforced aluminum matrix nanocomposites in this research. Intermetallic compounds are also expected to form as a result of the milling process such as Al_2Cu, Al_3Mg_2, and Al_4C_3 in aluminum alloys cases [19-23].

In this study, Al-4.5Cu-1.5Mg powder was used as a matrix material and graphite was used as reinforcement material. AA2024 is one of the aluminum alloy series that have high mechanical properties and high thermal stability. The purpose of this research was to investigate the shaker mill technique to manufacture graphite-reinforced Al-4.5Cu-1.5Mg metal matrix nanocomposite. Sintering and mechanical properties were also investigated to determine the effects of the graphite and shaker mill technique.

2. Experimental

2.1. Material Preparation

Elemental powders as matrices were prepared with composition ratio as shown in Table 1 below:

Table 1. Al-Cu-Mg Matrix Composition

Materials	Al	Cu	Mg
Composition (wt.%)	Bal.	4.5	1.5

Graphite was used with compositions of 0.1, 0.5, 1, and 3wt%. All powders were produced by Zhok Material Technical Co., Ltd in China with specifications in Table. 2 as follows:

Table 2. Powder specifications

Powder	Specification (purity and mesh)
Al	99%, 320 mesh
Cu	99.5%, 500 mesh
Mg	99%, 320 mesh
Graphite	99.5%, <20μm

The theoretical density of compounds was calculated by using the formula below:

$$\rho_t = \frac{(m_a + m_b)}{\left(\frac{m_a}{\rho_a} + \frac{m_b}{\rho_b}\right)} \quad (1)$$

where m_a and m_b are the mass of each element, ρ_a and ρ_b are the theoretical density of each element in the alloy.

And the morphology of graphite is shown below;

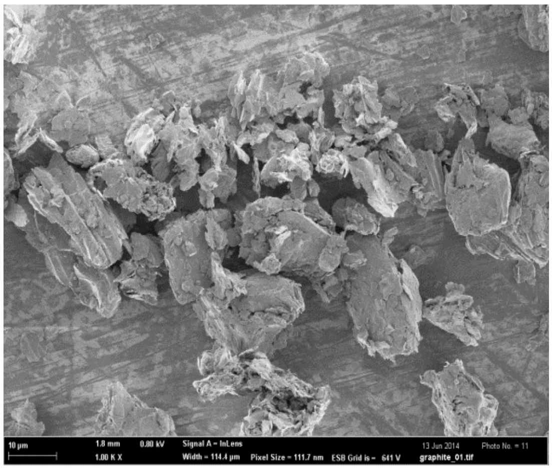

Fig. 1 Morphology of graphite

The powders were milled in a shaker mill with the ball-to-powder weight ratio of 10:1 under argon gas for 8 hours at 750 rpm. A ceramic ball mill and Teflon or polytetrafluoroethylene jar were used during milling.

Milled powder was compacted with single action press at 500 MPa. Stearic acid was added for 1.5wt% of the total weight to the powder specimen as a lubricant to reduce friction during the compaction process. Green density was measured by measuring dimension and mass. Sintering was carried out under ultra-high purity argon gas at 550°C, 580°C, 600°C, and 620°C. Sintering density was obtained by using the Archimedes method.

2.2. Microstructure and Characterization

Particle size analyzing (PSA) test was used to measure the particle size distribution of nanocomposite powder after the shaker mill process. This process used isopropanol as a solvent and is carried out at room temperature using PSA equipment.

A scanning electron microscope (SEM) was used to characterize the morphology of the powder. SEM instrument with vacuum measurement parameters of 20 kV and 50 intense spots.

To characterize the thermal properties of the powder and estimate the optimal temperature for the sintering process, DSC-TGA was used using 99.999% ultra-high purity argon gas with a temperature of 20-800°C and a heating rate of 10°K / minute.

2.3. Density and Hardness Test

Vickers hardness tests were carried out to investigate mechanical properties. using Vickers microhardness tool with ASTM E92-16 standard. The sintering density samples were measured by Archimedes principle according to ASTM B961 standard and calculated by the following formula:

$$\rho_s = \frac{w_{air}}{w_{air} - w_{water}} \cdot \rho_{water} \qquad (2)$$

3. Result and Discussion

3.1. Powder Characterization

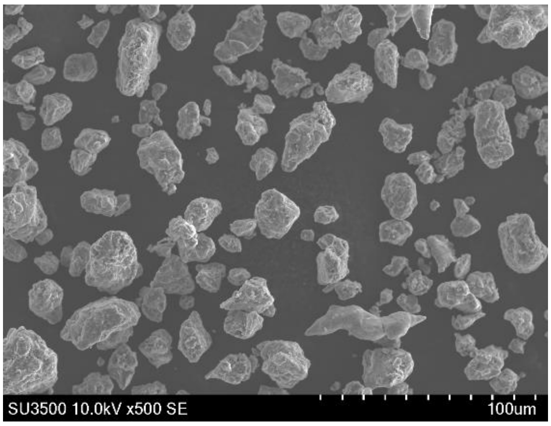

Fig. 2. Particle morphology of Al-4.5Cu-1.5Mg with 0.5wt% graphite after shaker mill process.

The powder was characterized to identify its morphology as shown in Fig 2. The Figure shows the irregular shape of the powder. The irregular shape of the particles has the advantage during the compacting process. Because when compressing, the powder is able to fill almost all voids between them leading to lower porosity meaning it is easier for sintering. Damaging, fracturing, and cold welding happened during the shaker mill at such a shorter time. Due to high-speed milling, the cold welding process is applied when all elementals will be diffused from each other to form intermetallics.

According to particle size analyzer results shown in Table 3, it shows that the average particle diameter after 8 hours of shaker mill was 112.521 nm. This result shows that the shaker mill technique was able to produce graphite-reinforced Al-4.5-1.5Mg nanocomposite. But the range between D 10%, D 50%, and D 90% shows non-homogenous particle size. Agglomeration of nanoparticles is still remained a challenge to characterize the particle size of the nanoparticle.

Table 3. particle size distribution of Al-4.5Cu-1.5Mg with 0.5wt% graphite nanocomposite

Material	Average Diameter (nm)	D 10% (nm)	D 50% (nm)	D 90% (nm)
Al-4.5Cu-1.5Mg with 0.5wt% graphite	112.521	29.501	74.934	102.380

Investigating the thermal properties of this powder is very important in order to be able to estimate the optimal temperature for sintering and to know the delubrication temperature.

Figure 3 shows DSC-TGA curves of Al-4.5Cu-1.5MG with 0.5wt% graphite nanocomposites. From the DSC curve (blue line), it can be seen when the phase transformation occurs from the exothermic and endothermic reactions. At a temperature of 477°C is the exothermic reaction where oxide removal reaction occurred.

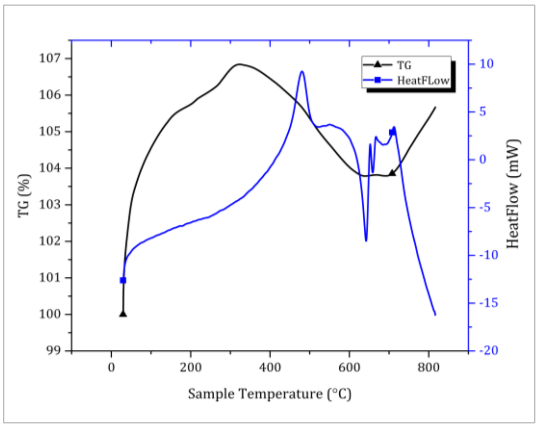

Fig. 3. DSC-TGA Curves of Al-4.5Cu-1.5Mg with 0.5wt% graphite nanocomposite

This reaction breaks the oxide layer on aluminum powder due to its high thermal expansion compared to the oxide layer. High internal pressure in aluminum at high temperatures is able to break the oxide layer on its surface. And this is beneficial for the sintering of aluminum powder, due to the high melting point of the oxide layer, it can prohibit the diffusion process during sintering between aluminum particles. With continued heating a strong endothermic peak appears at around 650°C, indicating the melting of the matrix alloy. At the TGA graph (black line), it seems the mass of powder decreased starting from 300°C to 600°C, indicated is a stearic acid that evaporates. The addition of stearic acid as a lubricant to the powder aims to reduce the friction in the compacting process so that no slip occurs which can affect diffusivity during sintering.

To see the phase transformation after the shaker mill process, x-ray diffraction was carried out as shown in Figure 4.

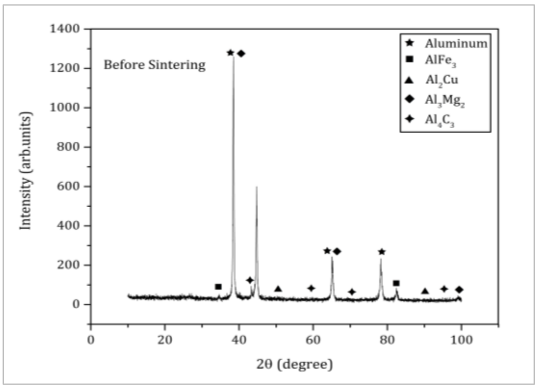

Fig. 4. X-Ray Diffraction Pattern of Al-4.5Cu-1.5Mg with 0.5wt% graphite nanocomposite after shaker mill

The graph shows the dominant peaks are Aluminum. In addition, the shaker mill process produces several intermetallic compounds such as Al_3Mg_2 and Al_2Cu which is advantageous due to its strong mechanical properties leading to better mechanical properties of the matrix [24]. AlF_3 was found as one of the impurities coming from shaker mill equipment. The jar is made with polytetrafluoroethylene material which expected fluorine will be one of the impurities for this nanocomposite powder but the effects of fluorine on the properties of nanocomposite powder is still a question. Aluminum carbide, Al_4C_3 was found as result coming from the reaction between aluminum and graphite during the shaker mill. It was also expected to form Al_4C_3 after a high-energy ball mill which was shown by researchers. Al_4C_3 acts as an interface between the matrix and reinforcement and is able to receive load or stress coming to the matrix and leading to better mechanical properties of the matrix [16]. The formation reaction of Al_4C_3 is as follows;

$$4Al + 3C \rightarrow Al_4C_3 \quad (3)$$

3.2. Green Compact Characteristic

From Figure 5 it can be seen that the best green density is in the graphite fraction of 0.5wt% which is equal to 73.7% relative. Green density started to low at 1 and 3wt% graphite. One of the main reasons is agglomeration between graphite particles. The challenge of dispersion of graphite at higher content will lead to limited application of graphite-reinforced aluminum matrix nanocomposite. In the sintering of aluminum powder, green density plays an important role in getting high sintering and mechanical properties. Some researchers showed that high green density leads to high sintering and mechanical properties.

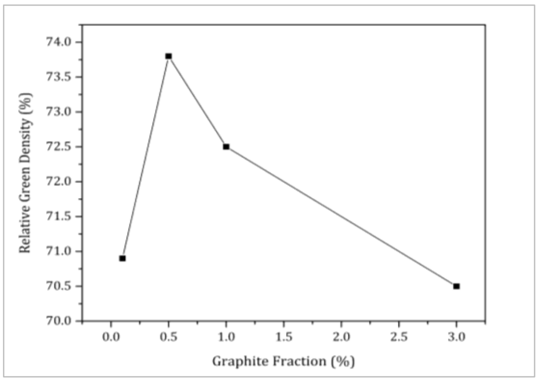

Fig. 5. Green density of graphite reinforced Al-4.5Cu-1.5Mg compacted at 500 MPa

3.3. Sintering Behavior

Sintering is the process of binding a compacted particle by using a thermal force below the melting point to produce high-density material. The sintering process of this powder was carried out at 550°C, 580°C, 600°C, and 620°C for 1 hour under ultra-high purity argon gas for 99.999%. Figures 6 a and b show the sintering behavior of graphite-reinforced Al-4.5Cu-1.5Mg matrix nanocomposite with variations of graphite and temperature respectively. Comparable to Figure 5, in Figure 6a, the optimum sintering density was obtained with 0.5wt% graphite for 77% relative.

The sintering temperature is also one of the important factors in the success of the sintering of aluminum powder. For this nanocomposite, it seems the most suitable sintering temperature is 550°C. According to DSC-TGA in Figure 3, the sintering temperature range can be predicted. Depending on chemical compositions, the optimum sintering temperature range is 550-600°C. One of the main challenges in obtaining higher sintering properties of graphite-reinforced aluminum matrix nanocomposite is the agglomeration of graphite particles. This agglomeration will cause porosity which leads to lower sintering properties and it shows on microstructures in Figure 7.

Porosity remains visible throughout the surface of the cross-section of the nanocomposite. From Figures 7a and 7b also some intermetallics are visible with white color. The intermetallic dispersed homogenously throughout the surface, inside and in between grain boundaries. Sintering at such high temperatures can facilitate some reactions between elements. At 620°C, there is grain growth with visible bigger grains. Too high sintering temperature will result in more porosity because of Ostwald ripening phenomena. This phenomenon occurs when particles diffuse each other at higher temperatures. Ostwald ripening leads to the dissolution of smaller solid grains, diffusion of the solute through the liquid, and the re-precipitation of the solid onto large grains [25].

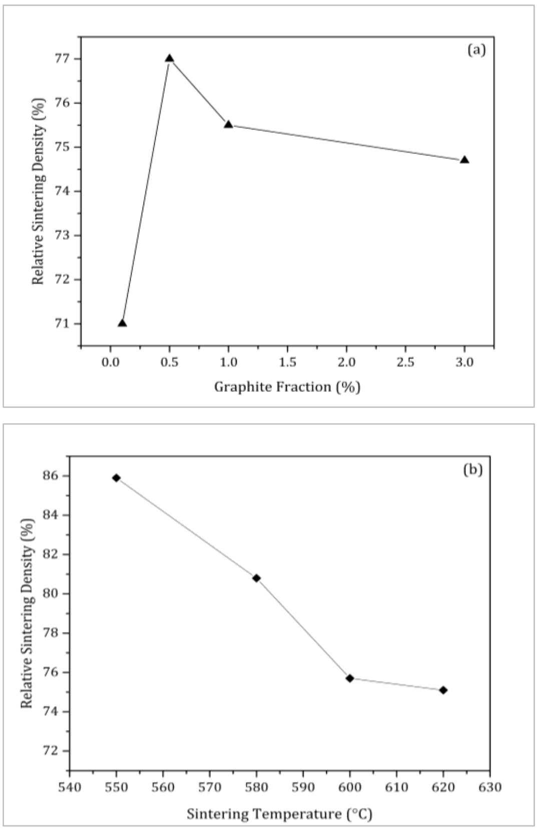

Fig. 6. a) Sintering density of Al-4.5Cu-1.5Mg with content of graphite for 0.1,0.5,1 and 3wt% sintered at 550°C and b) Sintering density of Al-4.5Cu-1.5Mg with 0.5wt% graphite sintered at 550°C, 580°C, 600°C, and 620°C

To investigate intermetallic phases during sintering, X-Ray Diffraction was carried out as shown in Figure 8. Aluminum is the dominant peak followed by the formation of intermetallics such as Al_2Cu, Al_3Mg_2, and aluminum carbide (Al_4C_3). Al_2Cu is a common intermetallic found in the aluminum-copper alloy. Al_2Cu after sintering has a stronger presence compared to after milling. this indicates high sintering temperatures facilitate the reaction between aluminum and copper to form Al_2Cu. Al_3Mg_2 has little presence compared to Al_2Cu due to its lower content on the alloy. The Al_4C_3 particles which were the primary precipitates in the aluminum–graphite played a major role in improving the mechanical properties. The presence of aluminum carbide (Al_4C_3) in these nanocomposites has the advantage of transferring the load between the matrix to the reinforcement, because of the fragile nature of aluminum carbide, the formation of aluminum carbide can increase aluminum rigidity. AlF_3 was also formed which was identified as an impurity. These impurities generally come from friction between the ball and the Teflon jar during the milling process.

Vickers hardness test was carried out to investigate one of the mechanical properties of this nanocomposite. Optimum Vickers hardness was obtained at 550°C sintering temperature for 159.4 HVN and decreased as the sintering temperature goes up as shown in Table 4. This indicates that hardness and sintering density have some correlation with determining the sintering properties of the aluminum nanocomposite. To determine how the Vickers hardness test was carried out, Figure 8 shows 5 indentation marks on this nanocomposite sintered at 550°C. A high number hardness number will decrease the area of the indentation mark meaning it has high resistance to permanent deformation.

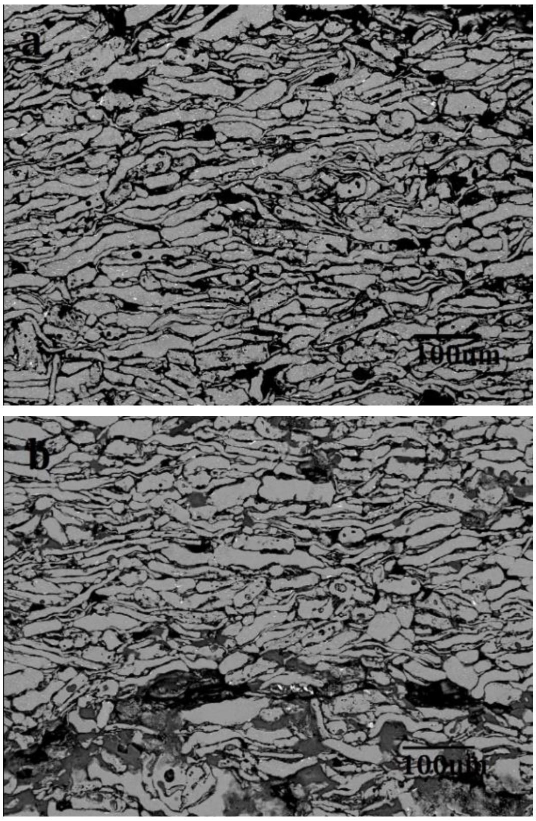

Fig. 7 Microstructure image of Al-4.5Cu-1.5Mg with 0.5wt% graphite nanocomposite sintered at a) 550°C and b) 620°C

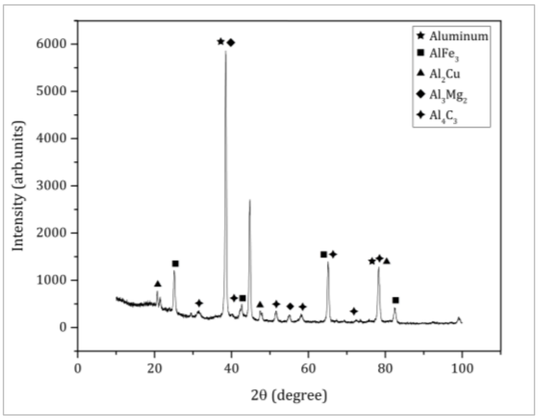

Fig. 8. X-Ray diffraction pattern of Al-4.5Cu-1.5Mg with 0.5wt% graphite nanocomposite after sintering at 550°C

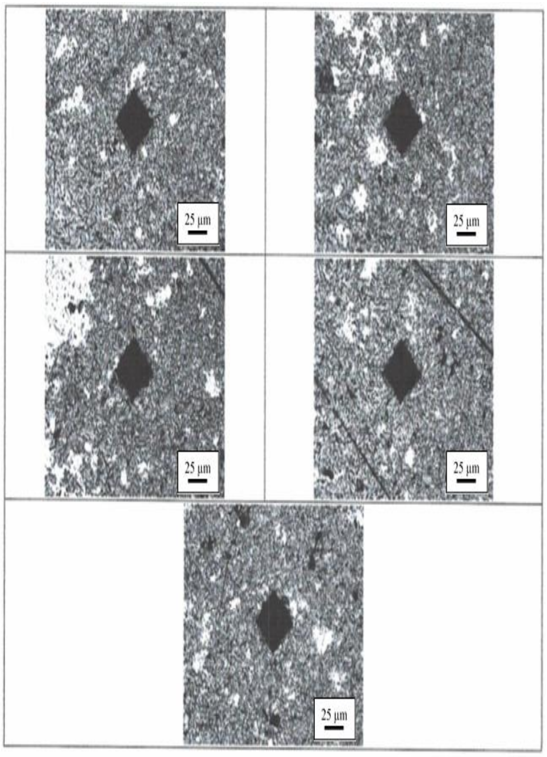

Fig. 9 Vickers hardness indentation of Al-4.5Cu-1.5Mg with 0.5wt% graphite nanocomposite sintered at 550°C

Table 4. Vickers hardness value to compacting pressure of the nanocomposites

Number	Sintering Temperature (°C)	Average Hardness Value (HVN)	Vickers Load (HVN)
1	550	159.4	5
2	580	143	5
3	600	115.8	5
4	620	76.4	5

4. Conclusions

In short, this research was successfully able to produce graphite-reinforced Al-4.5Cu-1.5Mg matrix nanocomposite by the shaker mil technique. 0.5wt% graphite seems to be the most suitable graphite content for Al-4.51.5Cu powder. Sintering under ultra-high purity argon gas for 99.999% was able to produce high-density nanocomposite which was able to reach 77% sintering density at 550°C. Intermetallics were found before and after sintering such as Al_2Cu, Al_3Mg_2, and Al_4C_3. Al_4C_3 was found as a result of the reaction between aluminum graphite, it acts as an interface between matrix and reinforcement particles. AlF_3 was found as an impurity due to an unnecessary reaction during the shaker mill between jar, ball, and powder. And optimum Vicker hardness was also obtained at 550°C sintering temperature and 0.5wt% graphite for 159.4 HVN.

Acknowledgments

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Conflicts of Interest

The author declares that there is no conflict of interest regarding the publication of this manuscript. In addition, the authors have entirely observed the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy.

References

[1] Lai, M.O., Lu, L. and Laing, W., 2004. Formation of magnesium nanocomposite via mechanical milling. *Composite structures*, *66*(1-4), pp.301-304.

[2] Pandya, S., Jani, S., Chavan, A., Singh, A.K., Bhatt, S., Patel, D., Bhatt, B., Patel, A., Girma, A. and Naik, K., 2013. Nanocomposites and IT'S application-review. *International Journal of Pharmaceutical Sciences and Research*, *4*(1), pp.19-28.

[3] Surappa, M.K., 2003. Aluminium matrix composites: Challenges and opportunities. *Sadhana*, *28*(1-2), pp.319-334.

[4] Veličković, S., Garić, S., Stojanović, B. and Vencl, A., 2016. Tribological properties of aluminium matrix nanocomposites. *Applied Engineering Letters*, *1*(3), pp.72-79.

[5] Hassan, A.M., Alrashdan, A., Hayajneh, M.T. and Mayyas, A.T., 2009. Wear behavior of Al–Mg–Cu–based composites

containing SiC particles. *Tribology International*, *42*(8), pp.1230-1238.

[6] Koli, D.K., Agnihotri, G. and Purohit, R., 2015. Advanced aluminium matrix composites: the critical need of automotive and aerospace engineering fields. *Materials Today: Proceedings*, *2*(4-5), pp.3032-3041.

[7] Saboori, A., Dadkhah, M., Fino, P. and Pavese, M., 2018. An overview of metal matrix nanocomposites reinforced with graphene nanoplatelets; mechanical, electrical and thermophysical properties. *Metals*, *8*(6), pp.423.

[8] Jawalkar, C.S., Verma, A.S. and Suri, N.M., 2017. Fabrication of aluminium metal matrix composites with particulate reinforcement: a review. *Materials Today: Proceedings*, *4*(2), pp.2927-2936.

[9] Suryanarayana, C., 2001. Mechanical alloying and milling. *Progress in materials science*, *46*(1-2), pp.1-184.

[10] Taha, M.A., Youness, R.A. and Zawrah, M.F., 2019. Review on nanocomposites fabricated by mechanical alloying. *International Journal of Minerals, Metallurgy, and Materials*, *26*(9), pp.1047-1058.

[11] Zebarjad, S.M. and Sajjadi, S.A., 2006. Microstructure evaluation of Al–Al2O3 composite produced by mechanical alloying method. *Materials & design*, *27*(8), pp.684-688.

[12] Wagih, A., 2015. Mechanical properties of Al–Mg/Al2O3 nanocomposite powder produced by mechanical alloying. *Advanced Powder Technology*, *26*(1), pp.253-258.

[13] Brooks, J.D. and Taylor, G., 1965. The formation of graphitizing carbons from the liquid phase. *Carbon*, *3*(2), pp.185-193.

[14] Ravindran, P., Manisekar, K., Narayanasamy, P., Selvakumar, N. and Narayanasamy, R., 2012. Application of factorial techniques to study the wear of Al hybrid composites with graphite addition. *Materials & Design*, *39*, pp.42-54.

[15] Sherif, E.S.M., Almajid, A.A., Latif, F.H. and Junaedi, H., 2011. Effects of graphite on the corrosion behavior of aluminum-graphite composite in sodium chloride solutions. *Int. J. Electrochem. Sci*, *6*, pp.1085-1099.

[16] Yu, Z., Bai, Y., Wang, J. H., Li, Y., 2021. Effects functional additives on structure and properties of polycarbonate-based composites filled with hybrid chopped carbon fiber/graphene nanoplatelet fillers. *ES Energy and Environment*, 12, pp 66-76.

[17] Kachere, A. R., Kakade, P. M., Kanwade, A. R., Dani, P., Mandlik, N. T., Rondiya, S. R., Dzade, N. Y., Jadkar, S. R., Bhosale, S. V., 2022. Zinc Oxide/Graphene Oxide Nanocomposites: Synthesis, Characterization and Their Optical Properties. *ES Materials and Manufacturing*. 16, pp. 19-29.

[18] Shrivastava, Pankaj., Alam, Syed Nasimul., Maity, Taraknath., Biswas, Krishanu., 2021. Effect of graphite nanoplatelets on spark plasma sintered and conventionally sintered aluminum-based nanocomposites developed by powder metallurgy. *Materials Science-Poland*, 39(3), pp. 346-370.

[19] Molina-Boisseau, S. and Le Bolay, N., 2000. Size reduction of polystyrene in a shaker bead mill—Kinetic. *Chemical Engineering Journal*, 79(1), pp. 31-39.

[20] Estrada-Guel, I., Carreño-Gallardo, C., Mendoza-Ruiz, D.C., Miki-Yoshida, M., Rocha-Rangel, E., Martinez-Sanchez, R., 2009. Graphite nanoparticle dispersion in 7075 aluminum alloy by means of mechanical alloying. *Journal of Alloys and Compounds*, 483(1-2), pp. 173-177.

[21] Suryanarayana, C., 2011. Synthesis of nanocomposites by mechanical alloying. *Journal of Alloys and Compounds*, *509*, pp. S229-S234.

[22] Gorrasi, G. and Sorrentino, A., 2015. Mechanical milling as a technology to produce structural and functional bio-nanocomposites. *Green Chemistry*, *17*(5), pp.2610-2625.

[23] Rudianto, H., Jang, G.J., Yang, S.S., Kim, Y.J. and Dlouhy, I., 2015. Evaluation of sintering behavior of premix Al-Zn-Mg-Cu alloy powder. *Advances in Materials Science and Engineering*, *2015*.

[24] Zolriasatein, A., Khosroshahi, R.A., Emamy, M. and Nemati, N., 2013. Mechanical and wear properties of Al-Al_3Mg_2 nanocomposites prepared by mechanical milling and hot pressing. *International Journal of Minerals, Metallurgy, and Materials*, *20*(3), pp.290-297.

[25] S.H.Huo, M.Qian, G.B.Schaffer, E.Crossin., 2011. Aluminium powder metallurgy. *Fundamentals of Aluminium Metallurgy,* pp. 655-701.