



### Review Article

## INVESTIGATION OF SINTERING CONDITIONS AND THE GNP ADDITIONS ON ALUMINUM COMPACTS

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### ABSTRACT

Today, due to its lightness and superior properties, the use of Aluminum (Al) materials has increased considerably. In the production of Powder Metal (PM) or nanomaterials, it is possible to form the materials required by the additives to be added into the main composition. When recent studies investigated, it has been seen that the Graphene NanoPlate (GNP) additive improves the mechanical properties of almost all materials. In this review study, the properties of GNP added to Aluminum PM and Nanomaterials are investigated. Also, the mechanical properties of Al-GNP materials sintered with different methods such as hot pressing, hot extrusion, and plasma sintering are investigated and compared among themselves.

**Keywords:** Aluminum, GNP sintering, powder metal, nanomaterials.

### 1. INTRODUCTION

Aluminum (Al) element, which the raw material of many products, is a metal preferred by engineers in plenty of areas. Due to its lightness, flexibility, electrical, and thermal conductivity, processability Al materials are used in the cooling industry, construction sector, electronic devices and nearly all of the vehicles.[1,2,3]

A nanometer is about one-millionth of a millimeter. In order to define a material as a nanomaterial, at least one dimension must be less than 100 nanometers. These materials have superior electrical, optical and magnetic properties. As a result of these properties, nanomaterials are used in plenty of sectors such as biomedical, electronic, energy, textile.[4]

With the increasing industrialization, the materials and machine parts produced by the classical methods cannot meet the requirements. For this reason, studies to provide higher performance and functional materials have increased. With the introduction of nanotechnology into human life, these studies produced different results, and new materials were used. With the introduction of nanotechnology into human life, these studies have given varying results, and new materials were produced. GNP is one of the nanomaterials found in these investigations.[5]

GNP is a layered of carbon atoms arranged in a honeycomb lattice in two dimensions and layered structure of clays with superior properties of carbon nanotubes. The layers are high strength, electronic conductivity, large specific surface area, etc. [6,7,8,9,10]

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During the manufacturing process, some small parts cannot be manufactured due to the difficulty of production. Modern production methods are used to produce these parts. In these methods, the number of wastages is low, but the manufacturing is slow. Powder Metallurgy method has been developed to accelerate production and to reduce the amount of wastage. In powder metallurgy, primarily raw materials are pulverized through some processes. After that, the powders obtained can be used as a need for alloy or reinforcing elements. After adding various binders into the powdered alloy, they are poured in the molds, pressed and sintered. Sintering is a heat treatment applied in powder metallurgy. This heat treatment is made by pouring the powder mixture into the mold and forming a chemical bond between the powders by heating to a temperature below the melting temperature. The aim is to develop the properties of the material at the macro level. In the sintering process, mechanical bonds formed by the pressing process grow stronger with chemical bonds.[11]

In this review study, hot pressing, hot extrusion, and plasma sintering were used as a reference. Hot pressing is a suitable method for producing materials with high-performance materials and low sintering behavior. It has advantages of simultaneous application of temperature and pressure, production of well-microstructured materials and low cost. The disadvantage of hot pressing is the slow progress of the process and the difficulty of temperature control due to the mold accent used.[12]

Hot extrusion is one of the most popular methods to develop objects. Hot extrusion is the process of pushing the material into molds at high temperatures. It is easy to make changes in this production because the product is still hot after the application. Many types of raw materials can be used, and high surface quality products are obtained. Disadvantages of this method are the contact of the metal with the atmosphere may cause unwanted reactions after the process and high cost. [13,14]

Plasma sintering is a novel technique that pulsed or unpulsed DC or AC current directly passes through the graphite die. In this method, the sample gets warm from the inside. The plasma sintering method has advantages such as higher sintering speed and lower sintering temperature than other traditional sintering methods. [15,16,17]

In this review study, the effect of GNP additive added to Al powders on the mechanical properties of aluminum materials were investigated. Also, the mechanical properties of Al-GNP materials sintered with different methods such as hot pressing, hot extrusion, and plasma sintering will be investigated and compared among themselves.

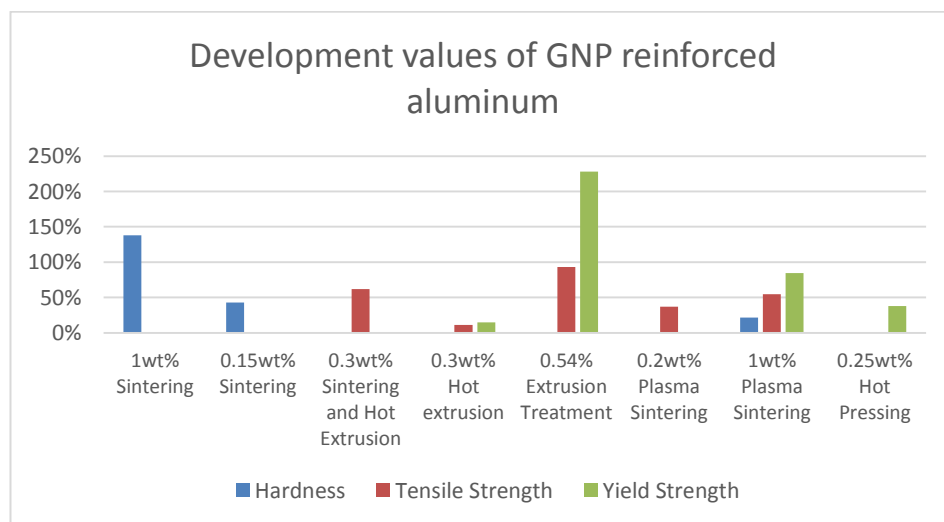
## **2. MATERIALS AND METHODS**

Eight different experimental setups were studied.

In this study, the effects of GNP particles added to pure aluminum powders in different wt% proportions were investigated. Also, three different production methods such as hot extrusion, sintering, and plasma sintering were examined and results were compared among themselves. The reviewed articles are given in Table 1 and Fig1.

**Table 1.** Development values of GNP reinforced aluminum

Study Number	Preparation Methods	GNP Amount	Matrix Alloy	Results	References
1	Sintering	1wt%	Pure Al	%138 increment in hardness	[18]
2	Sintering	0.15wt%	Pure Al	%43 increment in hardness	[19]
3	Sintering and Hot extrusion	0.3wt%	Pure Al	%62 increment in tensile strength	[20]
4	Hot extrusion	0.3wt%	Pure Al	%14.7 increment in yield strength, %11.1 increment in tensile strength	[21]
5	Extrusion treatment	0.54%	Pure Al	%228 increment in yield strength, %93 increment in tensile strength	[22]
6	Plasma sintering	0.2wt%	Pure Al	%36.8 increment in tensile strength	[23]
7	Plasma Sintering	1wt%	Pure Al	%21.4 increment in hardness, %54.8 increment in tensile strength, %84.5 increment in yield strength	[24]
8	Hot Pressing	0.25wt%	Pure Al	%38 increment in yield strength	[25]

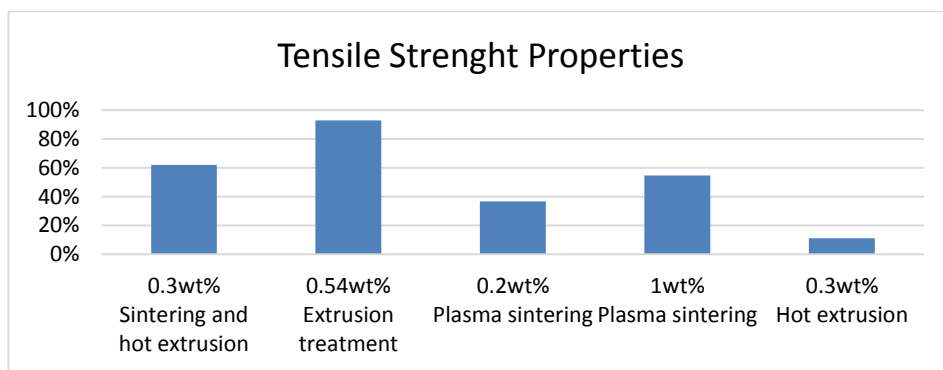
**Figure 1.** Development values of GNP reinforced aluminum

Bustamante et. al. in their study [18], GNPs and Al powder were placed in a vial made from a hardened steel tool and milling media made from hardened stainless steel. GNPs were added in 1.0 wt% into the aluminum matrix. The ball to powder ratio was set to 5:1. All milling runs were performed with methanol as a process control agent and argon atmosphere to avoid excessive agglomeration and oxidation, respectively. The milling times were of 5 h. Milled powders were coldly consolidated to form discs of 6.7 mm of diameter and 1 mm of height, under 950 MPa and then sintered under argon atmosphere during 2h at 500 °C with a heating and cooling rate of 5

°C/min. Liu et. al. in their study [19], 0.15wt% GNP additive added to the aluminum matrix. The effects of sintering conditions, e.g., atmosphere, temperatures, holding time and heating rate, were investigated and optimized. The horizontal tube furnace was used with the optimized sintering conditions of 5°C/min from room temperature to 600°C (~ 88% of the melting temperature of the pure aluminum powder), with a holding period of 4h and in an argon atmosphere. Wang et. al. in their study [20], PM compact with 0.3wt% GNP reinforcement sintered in an Ar atmosphere at 580 °C for 2 h, followed by hot extrusion at 440 °C with an extrusion ratio of 20:1. Rashad et. al. in their study [21], at first Graphene Nanoplatelets (GNPs) were ultrasonicated in acetone for 1h. Graphene Nanoplatelets (GNPs) with particle contents of 0.3 wt% were slowly added to the aluminum powder slurry in acetone. The mixing process was continued for one hour using a mechanical agitator to obtain the homogeneity in the mixture. The composite powder was compacted in a stainless-steel mold at room temperature under the pressure of 170 MPa to obtain green billet with Ø30\_30mm dimensions. After compacting, the green billets were sintered in a muffle furnace at 600 °C for 6 h followed by hot extrusion at 470 °C to obtain the rods of 16 mm diameter. Yang et. al. in their study [22], The GNPs were firstly mixed with pure Al powder using a planetary mill at a rotation speed of 100 rpm for 1 h. The mixture was then put into a steel mold and further pressed to the set height to prepare the preforms, and the volume content of the milled particles in the mold was about 60 vol.% to 70 vol.%. The preheating temperatures for the preform and pressure infiltration dies were 500 and 730 °C, respectively. During the infiltration process, a pressure of 15 MPa was applied and maintained for 5 min, GNPs in the GNPs/Al composites have been calculated to be 0.54 wt.%. Afterward, in order to investigate the effect of the extrusion treatment, parts of samples were extruded at 450 °C with the extrusion ratio of 11:1. Li et. al. in their study [23], 0.2wt% GNP additive added to the aluminum matrix. Al-GNPs powders were consolidated by spark plasma sintering (SPS) with a pressure of 50 MPa at 500 °C. The mixed Al and GNPs powders were then cold-pressed and the cold-pressed mix powder was called Al-GNPs master alloy and was added into aluminum melts heated with electromagnetic induction furnace with a mass proportion of 1: 9. Bisht et. al. in their study [24], the powder was then sintered in an inert argon atmosphere in spark plasma sintering furnace. Al-GNP composite, maximum pressure, and temperature used were 50 MPa and 550°C, respectively, withholding time of 40 minutes. Compositions with reinforcement content. GNP reinforcement was 1wt%. Li and Xiong in their study [25], GNPs were added in 0.25wt% into the aluminum matrix. In order to disperse uniformly the GNPs in Al matrix, the ultrasonic processing was employed, which vibrates at a frequency of 35 kHz for 40 min. The GNPs were added in ethanol, and ultrasonic processing was carried out for about 45 min. The GNPs-Al mixtures were mixed by high-energy ball milling for 4 h in high purity (> 99.99%) argon atmosphere to avoid element oxidation. The weight ratio of the ball to the mixture was 10:1. The rotational speed was controlled at 250 rpm. The GNPs-Al mixtures were dried under vacuum at 80°C for 24 h. The samples were hot-pressed sintered at 610°C for 4h under pressure of 30MPa in a vacuum.

**Table 2.** Tensile strength properties

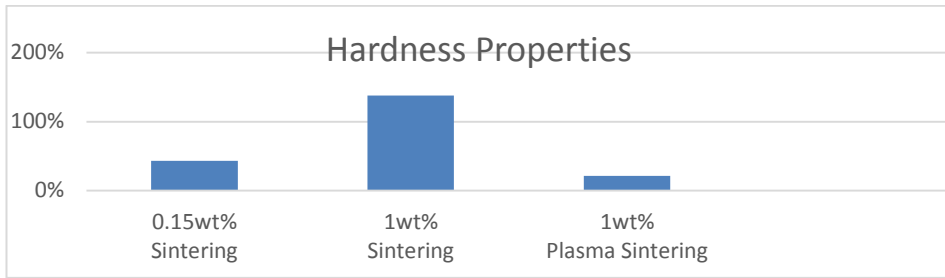
Study Number	Preparation Methods	GNP Amount	Matrix Alloy	Results	References
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5	Extrusion treatment	0.54wt%	Pure Al	%93 increment tensile strength	[22]
6	Plasma sintering	0.2wt%	Pure Al	%36.8 increment in tensile strength	[23]
7	Plasma sintering	1wt%	Pure Al	%54.8 increment in tensile strength,	[24]
4	Hot extrusion	0.3wt%	Pure Al	%11.1 increment in tensile strength	[21]



**Figure 2.** Tensile strength properties

**Table 3.** Hardness Properties

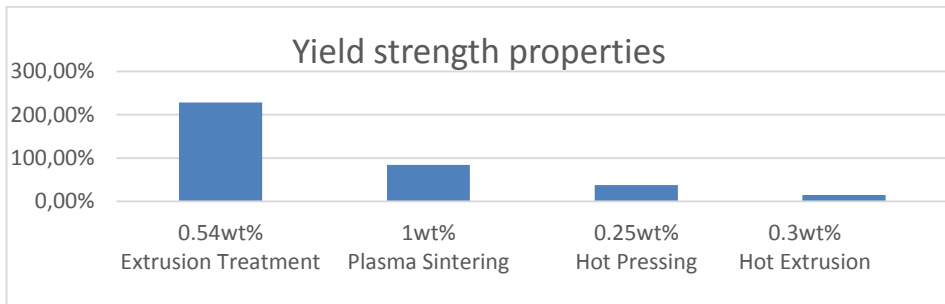
Study Number	Preparation Methods	GNP Amount	Matrix Alloy	Results	References
2	sintering	0.15wt%	Pure Al	%43 increment in hardness	[19]
1	sintering	1wt%	Pure Al	%138 increment in Hardness	[18]
7	plasma sintering	1wt%	Pure Al	%21.4 increment in hardness	[24]



**Figure 3.** Hardness Properties

**Table 4.** Yield strength properties

Study Number	Preparation Methods	GNP Amount	Matrix Alloy	Results	References
5	extrusion treatment	0.54wt%	Pure Al	%228 increment in yield strength	[22]
7	plasma sintering	1wt%	Pure Al	%84.5 increment in yield strength	[24]
8	hot pressing	0.25wt%	Pure Al	%38 increment in yield strength	[25]
4	hot extrusion	0.3wt%	Pure Al	%14.7 increment in yield strength	[21]



**Figure 4.** Yield strength properties

### 3. RESULTS

#### 3.1. Tensile Strength Properties

The representative table of increment in tensile strength was shown in Table 2. Tensile strength has increased in all samples. The minimum increase has seen in 0.3wt% GNP added, the hot extruded sample which had a %11.1 increment in tensile strength. The maximum increase has seen in 0.54wt% GNP added, the extruded sample which was %93 increment tensile strength.

Nothing but sintering was a powerful method but when sintering and extrusion processes were used together, it provides more efficient results with less GNP additive. In 0.4wt% GNP added and sintered sample which had a %52 increment in tensile strength. 0.3wt% GNP added, sintered and extruded sample which had a %62 increment in tensile strength.

The samples sintered by plasma sintering were examined. As the contribution of GNP increased, tensile strength was increased. In the sample of 0.2wt%, GNP added, plasma sintered sample which had a %36.8 increment in tensile strength. In the sample of 1wt%, GNP added, plasma sintered had a %54.8 increment in tensile strength.

Hot extrusion was the least effective method compared to others. 0.3wt% GNP added the hot extruded sample which had only a %11.1 increment in tensile strength. 0.5wt% GNP added, the hot extruded sample which had %17.7 increment in tensile strength.

### **3.2. Hardness Properties**

The representative table of increments in hardness was shown in Table 3. And Fig 2. Hardness increased in 3 samples. 0.15wt% GNP added the sintered sample had a 43% increment in hardness. 1wt% added sintered sample which had a %138 increment in Hardness. 1wt% GNP added plasma sintered sample which had a %21.4 increment in hardness.

### **3.3. Yield Strength Properties**

The representative table of increments in yield strength was shown in Table 4. The minimum increase has seen in. 0.5wt% GNP added the hot extruded sample which had a %228 increment in yield strength. The maximum increase has seen in 0.54wt% GNP added the extruded sample which had a %228 increment in yield strength. 1wt% GNP added plasma sintered sample which had a %84.5 increment in yield strength. 0.25wt% GNP added hot-pressed sample which had a %38 increment in yield strength. 0.3wt% GNP added the hot extruded sample which had a %14.7 increment in yield strength.

Differences in results may according to pre-sintering processes, sintering type, temperature, time and mass to GNP ratio. The uniform distribution of reinforcements is a good way to determine the load transfer property. Especially the extrusion method examined, there is a thermal expansion mismatch between the graphene and Al matrix. This mismatch acts on the matrix in the form of the pre-stress or may release the dislocation cycle. Graphene reinforcement can cause increased dislocation density. Increased dislocation density leads to increment in strength and at the same time increment in yield strength. Graphene atoms are spread along the grain boundaries of the Al matrix and strongly inhibit diffusion this is one of the reasons that increment in the strength. [26,27]

When the tables are examined, it is observed that tensile strength and yield strength increases as GNP additive up to 54% increases. When more than 54% is exceeded, the properties are fixed depending on the production method and GNP contribution by mass.

Compared to hot extrusion, extrusion and SPS at the same additive values, it has seen that extrusion provides more features increase. Comparing the hot pressing (HP) with SPS, it was suggested that the HP method was grain growth due to long waiting times at high temperatures. This negatively affects the strength of the material. On the other hand, there is no grain growth due to the rapid temperature rise and short sintering time in the SPS method. [28]

Four different production methods in yield strength have been studied with the contribution of GNP at different %wt's. There is a big difference between the result of the extrusion and the results of the other methods. When the production methods are compared with the same contribution values, the highest increase is seen in extrusion.

Hardness increment was investigated between SPS and sintering methods. It is seen that sintering provides more feature increment with lower GNP contribution.

#### 4. DISCUSSION AND CONCLUSION

In this study, GNP reinforcement in the range between 0.15wt% and 1wt% was added to the aluminum nanopowders. The effects of GNP contribution were investigated. The results obtained are as follows;

- The highest tensile strength value was obtained with a 0.54wt% GNP additive. It was observed that the addition of GNP reinforcement above 0.54wt% did not increase and decrease mechanical values. Since GNP is an expensive material, it should be optimally added to Aluminum nanopowders. 0.54wt% GNP additive is the optimum additive value for tensile strength.

- The highest hardness value was obtained with a 1wt% GNP additive. 1wt% GNP additive is the maximum additive value for tensile strength. If this value is exceeded, decrement can be seen on mechanical properties.

- The highest yield strength value was obtained with a 0.54wt% GNP additive. It was observed that the addition of GNP reinforcement above 0.54wt% did not increase and decrease mechanical values. 0.54wt% GNP additive is the optimum additive value for tensile strength.

- Besides, four different methods such as extrusion treatment, hot extrusion, SPS, conventional sintering were examined. For Al-GNP samples, hot extrusion is the method that increases the tensile strength the most.

- Two different methods such as conventional sintering and SPS were examined for hardness values. Conventional sintering is the method that increases the hardness most.

- Four different methods such as extrusion treatment, SPS, HP, hot extrusion were examined for yield strength values. Extrusion treatment is the method that increases the yield strength most.

When samples of the same GNP contribution percentages are examined: One of the samples with 1wt% GNP addition was produced in SPS and the other in the conventional sintering method.

- 138% hardness increment was observed in the sample produced by the conventional sintering method.

- %21.4 increment in hardness, %54.8 increment in tensile strength, %84.5 increment in yield strength was observed in the sample produced by SPS method.

One of the samples with 0.3wt% GNP addition was produced in conventional sintering and hot extrusion and the other in hot extrusion method.

- %62 increment in tensile strength was observed in the sample produced by sintering and hot extrusion.

- %14.7 increment in yield strength, %11.1 increment in tensile strength observed in the sample produced by hot extrusion.

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