The Effect of Al₂O₃ Nano Particles on Characteristics of Mg-Al-5TiB Grain Refiner Composites Produced by Stir Casting Method

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Abstract. High needs for light material with good mechanical characteristics made magnesium and its alloys as an alternative choice because of magnesium's low density, 1.74 gr/cm³. However, its use is limited by its low strength and ductility. In this experiment, a fabrication process of the composite which is Mg-Al-5TiB as Matrix with the addition of Nano Al₂O₃ as a reinforced with volume fraction varied from 0.10 Vf-% to 0.25 Vf-% by stir casting method. The composites then were characterized by both microstructure and mechanical properties. The microstructure was analyzed by an optical microscope and scanning electron microscope link to energy-dispersive spectra to analyze the phases present in composites and confirmed by X-Ray Diffraction. The XRD shows some phases such as Mg, MgO, MgAl₂O₄, and B₂O₃. The optimum mechanical properties of composites were obtained at the addition of 0.2 Vf-% Al₂O₃, where the tensile strength, elongation, wear rate and impact strength were 46.1 MPa, 14%, 0.3x10⁻⁵ mm/s, and 0.06 J/mm². The hardness of composites was value, 40.1 HRH. The porosity maximum was found at the addition of 0.25 Vf-% with the value of 9.37% caused by nano Al₂O₃ particle forming clustering (porosity is related to clustered particles) and inhibiting liquid metal moving rate. The addition of grain refiner makes solidification went faster and refined the grains.

Keywords: Magnesium Composite, Mg-Al-5TiB, Al₂O₃ Nano Particles, Stir Casting Method

1. Introduction
Indonesia is an active country in developing various industrial fields, such as the automotive industry, arms industry, manufacture, and infrastructure industry, etc. These developments reflect the development progress of a country, including the automotive industry. Along with the growth of the needs of the automotive market in Indonesia, the demands for more effective and efficient fossil fuels have also increased. By increasing fuel efficiency, the use of fuel for a vehicle can be saved and the pollution produced can be minimized. However, world oil conditions that are declining in capacity and its fluctuating prices and tight controls and efforts to reduce emissions in order to reduce environmental impacts are triggers the current industries to incessantly search for new materials as an alternative over conventional materials. Since the significant influence, the automotive industry gives to a country, one alternative is the choice of lightweight material as the main material. One of the light materials that can be used is Magnesium.

Magnesium is the lightest of all structural metals. Magnesium has a specific gravity of 1.74 g/cm³
[1], which is approximately one quarter of the weight of steel and two-thirds of aluminium. Moreover, the availability of magnesium in nature is very high since magnesium is the most abundant element of the sixth order on earth, 2.7% of the earth's crust composition is magnesium [2].

It has an HCP (Hexagonal Close Packed) structure so that it brings Magnesium to have highest specific strength. Magnesium as based metal matrix composites (MMCs) has attracted considerable interest because of their unique mechanical properties over monolithic alloy. This is due to the fact that monolithic alloys possess low elastic modulus. This limitation can be circumvented by incorporation of harder and stiffer ceramic particulates and alloying elements in the matrix. However, the selection of the type, size and volume fraction of particulates are essential to give the optimum properties to these composite materials. One of the reinforcements that can be used is the nano-sized aluminium oxide ceramic particle (Al₂O₃), also the addition of Al-5Ti-B as a grain refiner. Ceramic reinforcement has isotropic properties, excellent mechanical properties, chemical inertness properties, is stable at high temperatures, and its expansion coefficient can be controlled [3], thereby ceramic particles are considered fair for metal matrix composite fabrication. Al-5Ti-B can improve the mechanical property, reduce porosity, increase resistant of hot cracking, and change the structure [4]. Thus, Mg-Al-5Ti-B is used as the main matrix then reinforced by nano-sized Al₂O₃ particle.

Stir casting is the fabrication method selected in this research because of its advantages which are economical, easy, flexible, and can be used for production in large quantities that is very suitable to be applied in the automotive industry. However, this method has some difficulties such as the highly chemical activity of Mg, hardly uniform distribution of particles caused by agglomeration of the nano- Al₂O₃ if it does not stir well, the precipitating or floating reinforcing particle (depending on the specific gravity of the reinforcement phase and the metal matrix), the breaking of the reinforcing particles during the agitation process, the moisture between the particles and the matrix, and the porosity in the composite matrix. Therefore, a composite material with magnesium base matrix is developed with variation addition of nano-Al₂O₃ particles as reinforcement particle using a stir casting method to investigate the influence and mechanism of the number and shape of nano-Al₂O₃ reinforcing particles in improving the mechanical properties of magnesium matrix composites.

2. Experimental Method

2.1 Materials
In this research, pure magnesium 90% wt and Al-5Ti-B 10% wt was used as the matrix and nano-sized Al₂O₃ particle with 0.10, 0.15, 0.20, and 0.25 Vf-% was used.

2.2 Sample Preparation
The magnesium ingot and Al-5Ti-B (matrix) were sawn into small block form using miniband saw. After sawn, magnesium and Al-5-Ti-B are weighted as the same as the mass balance. Magnesium was cleaned with soap and 96% alcohol in order to remove the inclusion particle and oil that might be left on the surface. Al₂O₃ (reinforce) was agglomerated by ultrasonic vibrator within 380 seconds in order to remove inclusions while the furnace and the mold were coated with mixing thinner and zircon so that the furnace and the melt have high thermal resistance to avoid cracking. After that, the magnesium and Al-5-Ti-B were inserted into the furnace, before turning on the heater, they were fluxed in 6 minutes and drained with argon gas in 20 seconds. The matrix was melted at 650°C in the furnace and before being poured into the matrix, the reinforce were pre-heated at 900°C in the muffle furnace to remove the moist. After the preheat process, nano Al₂O₃ particle was inserted into molten Mg-Al-5Ti-B and then stirred for 1 minute to obtain a homogenous mixture. Then, they were poured into the mold and the mold was opened after the composite was solidified. Finally, this composite sample was being used for further characterization.

2.3 Characterization
2.3.1 Chemical Characterization. Chemical characterization was performed using Optical Emission
Spectroscopy (OES) to determine what elements were present in magnesium ingot samples and Mg-Al-5Ti-B composite with 0.10, 0.15, 0.20, and 0.25 Vf-% nano-Al2O3. Chemical characterization using OES is generated in elemental form and the amount of a particular area is large enough. Elements obtained are further analyzed in relation to variations in the addition of nano-Al2O3 and the process of the stirring casting method.

2.3.2 Mechanical Properties Characterization. Each sample was subjected to destructive testing (tensile, impact, hardness, and wear testing). Prior to the destructive test, each specimen was tested to find its actual density using a tool based on Archimedes Theory. The tensile test was conducted using the GoTech machine based on JIS Z2241 at room temperature. The impact test was carried out using the Charpy method at room temperature. The hardness test was completed using the Brinell test with HRH type. The wear test was executed using a pin-on-disk machine named Ogoshi by sliding a specimen into a harder material for a 100-meter sliding distance.

2.3.3 Microstructural Characterization. One sample which had optimum value was prepared by grinding using an abrasive paper with the machine automatically then polished with micron alumina paste on velvet cloth also automatically. After sample preparation was done, the microstructure characterization was conducted using optical microscope to observe microstructure and perform grain calculation, SEM with EDX integration to see topography of specimen in 3D, surface fracture of impact testing, element mapping, and analysis, XRD ad for composite specimen with value hard composite, composite reinforcement, and composite with the most reinforcing volume fraction underwent an XRD test to know the formed phase.

3. Result and Discussion

3.1 Chemical Composition

OES (Optical Emission Spectrometry) is a test to confirm the presence of elements in magnesium as-cast or non-reinforced magnesium as well as magnesium composite quantitatively. Thus, one will know the effect of the casting process on metal characterization.

Table 1. Chemical composition of Mg as-cast and Composite Material.

| Element | Mg as-cast (%) | Mg-Al5TiB/0.10 Vf-% nano Al2O3 | Mg-Al5TiB/0.15 Vf-% nano Al2O3 | Mg-Al5TiB/0.20 Vf-% nano Al2O3 | Mg-Al5TiB/0.25 Vf-% nano Al2O3 |
|---------|----------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Mg      | >96.6          | 95.5                          | 93.8                          | >96.0                         | 95                            |
| Al      | 1.96           | 3.88                          | 5.45                          | 3.37                          | 4.29                          |
| Ti      | 0.00087        | 0.0536                        | 0.0782                        | 0.0565                        | 0.0692                        |
| B       | 0              | >0.0264                       | >0.0264                       | >0.0264                       | >0.0264                       |
| Be      | 0.00007        | 0.00028                       | 0.00041                       | 0.00023                       | 0.00022                       |
| Cu      | 0.0007         | <0.00010                      | <0.00010                      | <0.00010                      | <0.00010                      |
| Mn      | 0.0073         | 0.0134                        | 0.0167                        | 0.0113                        | 0.0125                        |
| Zn      | 0.0152         | 0.0484                        | 0.0336                        | 0.0218                        | 0.0224                        |
| Ag      | 0              | 0.0003                        | 0.00048                       | 0.00036                       | 0.00038                       |
| Ca      | 0              | 0.0012                        | 0.0018                        | 0.0012                        | 0.0021                        |
| Cd      | 0.00001        | <0.00010                      | <0.00010                      | <0.00010                      | <0.00010                      |
| Sn      | 0.0333         | 0.0398                        | 0.0548                        | 0.035                         | 0.34                          |
Table 1 above shows the chemical composition of the materials. According to characterization, magnesium as-cast has 96.6% Mg, which indicates that there is still a possibility of composition level up to 99% in accordance with the mass balance at the beginning. Instead, there are other elements that were not supposed to be in the composite, which are Al, Ti, Be, Cu, Mn, etc in a tiny amount. Nonetheless, these elements would not give a significant effect on the characteristics itself. For the composite, the result shows that the increase of reinforcing particles reduces the content of magnesium, while it decreases on the 0.20 and 0.25 Vf-% nano Al₂O₃. It was caused by the agglomeration, also while pouring the liquid into the mold was not fast enough so that the liquid composite reacted too long with the air.

3.2 SEM and EDS
SEM and EDS tests were performed using magnesium as-cast and magnesium composite with 0.20 Vf-% to represent all of the composite samples.

![Figure 1. The SEM result of Mg as-cast.](image)

**Table 2.** The EDS result of Mg as-cast.

| Points | Mg (%) | Al (%) | Si (%) | O (%) | Possible formed phase |
|--------|--------|--------|--------|-------|-----------------------|
| 002    | 100    | -      | -      | -     | Mg                    |
| 004    | 79.44  | 7.9    | -      | 12.66 | MgO, Al₂O₃             |
| 005    | 100    | -      | -      | -     | Mg                    |
| 006    | 85     | -      | 2.83   | 12.16 | MgO                   |

Based on Figure 1 and Table 2 above, they show some elements like Mg, Al, Si, and O which probably formed some compounds; MgO an Al₂O₃. MgO was formed due to the magnesium property which is very easy to react with air. Furthermore, Al₂O₃ was formed at point 004, it was caused by the presence of inclusions. Also based on the OES result, it shows that Mg as cast indeed has 1.96% Al.
Figure 2. The SEM result of Mg-Al-5Ti-B/ nano Al₂O₃ 0.20 Vf-%.

Table 3. The EDS result of Mg-Al-5Ti-B/ nano Al₂O₃ 0.20 Vf-%.

| Point | Mg   | Al   | Ti   | B    | O    | C    | Possible formed phase                        |
|-------|------|------|------|------|------|------|---------------------------------------------|
| 007   | 36,57| 3,69 | 0,18 | 9,54 | 48,7 | 1,23 | MgO, Al₂O₃, B₂O₃, MgAl₂O₄, Al₁₂Mg₁₇       |
| 008   | 14,65| 1,6  | 5,89 | 16,82| 53,45| 6,44 | MgO, Al₂O₃, MgAl₂O₄, Al₁₂Mg₁₇, B₂O₃, TiO₂   |
| 009   | 57,68| 1,08 | -    | -    | 39,14| 1,4  | MgO, Al₂O₃                                  |
| 010   | 24,81| 1,11 | 0,05 | 16,84| 54,74| 2,39 | MgO, Al₂O₃, MgAl₂O₄, Al₁₂Mg₁₇, B₂O₃, TiO₂   |
| 011   | 47,79| 3,22 | 0,33 | 3,85 | 43,2 | 1,5  | MgO, Al₂O₃, MgAl₂O₄, Al₁₂Mg₁₇, B₂O₃, TiO₂   |
| 013   | 30,89| 2,94 | 0,09 | 12,87| 51,7 | 1,31 | MgO, Al₂O₃, Mg₂Al₂O₄, Al₁₂Mg₁₇B₂O₃, TiO₂    |
| 014   | 35,72| 2,98 | 10,15| 4,41 | 43,09| 3,34 | MgO, Al₂O₃, MgAl₂O₄, Al₁₂Mg₁₇, TiO₂, B₂O₃  |
| 015   | 100  | -    | -    | -    | -    | -    | Mg                                            |
| 016   | 35,15| 1,05 | 0,03 | 11,91| 50,59| 1,2  | MgO, Al₂O₃, MgAl₂O₄, Al₁₂Mg₁₇, TiO₂, B₂O₃   |
| 017   | 21,88| 2,18 | 0,22 | 16,91| 54,17| 4,47 | MgO, Al₂O₃, MgAl₂O₄, Al₁₂Mg₁₇, TiO₂, B₂O₃   |

According to Figure 2 and Table 3 above, they identified 10 locations. Almost at all points, they had Mg, Al, O, Ti, and B which many compounds formed such as MgO, Al₂O₃, MgAl₂O₄, Al₁₂Mg₁₇, B₂O₃, and TiO₂. MgO as the rust product and showed at all points, this is because magnesium is a highly reactive metal and very easily oxidized. At point 013, TiO₂ formed is based on its
morphology that looks like a straight line. At location 007 was a little bit different, because it might show Al$_{12}$Mg$_{17}$ as dendrite. In addition, there was C element at almost all points, C was indicated as an impurity which can only form from a stirrer that might have rust.

3.3 XRD

XRD is a test to find out what phases are formed in the composite microstructure. In this research, magnesium composite with Al$_2$O$_3$ 0.20 Vf-% was observed to represent all the composite samples.

![XRD Graph](image)

**Figure 3.** The X Ray Diffraction of Mg-Al-5Ti-B reinforced 0.20 Vf-% nano Al$_2$O$_3$ composites.

Based on the Figure 3, there were 16 peaks at $\theta$ which are 13,2612; 19,5809; 26,68; 34,3753; 35,6481; 36,5975; 40,7468; 44,1643; 44,6572; 47,9456; 57,7107; 63,3855; 64,4163; 69,0999; 82,1061; 70,4862, dan 84,6962. The highest scores were Mg; MgO; MgAl$_2$O$_4$; B$_2$O$_3$. Mg phase had the highest peak amongst all with a score of 41. This indicates magnesium as a matrix has the dominant phase. After the Mg phase, there was a MgO phase with a score of 28 which signified magnesium properties that is very easy to react with air. There was a B$_2$O$_3$ phase, where boron will react with oxygen easily at a very high temperature and at the end form B$_2$O$_3$. Also, there was a MgAl$_2$O$_4$ phase which is a reaction between Mg and nano Al$_2$O$_3$ with a score of 7. The presence of reinforcement particles in magnesium composites will make magnesium composites much better than as-cast magnesium.

3.4 Microstructure

The observation used a digital optical microscope with 200x, 500x, and 1000x magnification. All samples were taken from the tensile test specimens and were prepared metallographically.
Figure 4. Microstructure images of (a) as-cast 200x; (b) Mg-Al5TiB/Nano Al2O3 0.10 Vf-%; (c) Mg-Al5TiB/Nano Al2O3 0.15 Vf-%; (d) Mg-Al5TiB/Nano Al2O3 0.20 Vf-%; (e) Mg-Al5TiB/Nano Al2O3 0.25 Vf-% 1000x.

Based on Figure 4, all samples appeared to have block spots which indicate the presence of impurity as well as porosity. The highest amount of corrosion and impurities were found in composite nano Al2O3 0.25 Vf-%. The impurity and porosity were caused by the presence of metal oxides formed during the stirring process [5]. Magnesium as-cast has a different morphology than the composite, it was white and oval-shaped. The oval shape was produced when the metal was poured and filled the mold. The wall part of the mold was the first area touched by the liquid so that the cooling rate was fast and became the initial freezing area. Magnesium composite has an equiaxed grain shaped [6]. It was caused by the addition of Al-5Ti-B as grain refiner which would affect its microstructure [4].

As we can see from the microstructure, there was no twinning phenomenon. It was caused by the addition of grain refinement agent Al-5Ti-B as much as 10 wt% which was able to prevent the formation of twinning in the grain boundary and form finer and random grains, thereby the material required larger force to form twinning [7]. There was dendrite in almost all microstructure. It was formed often in cast metal products. The rate of cooling is the most important factor for dendrite formation. The mechanical properties will increase in parallel with dendrite reduction [8].

3.5 Mechanical Properties
All samples were prepared and tested to measure mechanical properties (tensile strength, hardness, wear rate, impact strength) and density. Before performing destructive test, each specimen were tested to find its density using Archimedes’ Theory.

3.5.1 Tensile and Elongation
Figure 5. Mechanical properties of Mg-Al-5Ti-B reinforced 0.20 Vf-% nano Al₂O₃ composites (a) Tensile, and (b) Elongation.

Based on Figure 5, the highest tensile strength achieved in the addition of nano Al₂O₃ 0.20 Vf-% and the lowest is at nano Al₂O₃ 0.10 Vf-%. The increase of tensile strength is due to the addition of Al₂O₃ and Al-5Ti-B which act as a barrier from dislocation. The nano-size of Al₂O₃ makes the particle has a greater surface area than the micron size and it is effective to inhibit dislocation [9]. The tensile strength affects the elongation of the composite. The optimum level is shown at 0.20 Vf-% which is 14%. However, the nano-size particle of reinforcing will not give significant value for elongation, yet for tensile strength without decreasing the elongation itself [9].

3.5.2 Hardness, Wear rate and Impact

Figure 6. Mechanical properties of Mg-Al-5Ti-B reinforced 0.20 Vf-% nano Al₂O₃ composites (a) Hardness, (b) Wear rate, and (c) Impact Strength.
According to Figure 6, as the Al₂O₃ and Al-5Ti-B added increased, the hardness of cast increased as well. The maximum hardness is obtained by adding nano Al₂O₃ 0.25 Vf-%. The addition of nano-sized particles would trigger the formation of fine interphase so that it eases the transfer loading process. The hardness will influence the composite’s wear rate. The harder the material, the higher the wear rate, as shown that nano Al₂O₃ 0.25 Vf-% had the lowest wear rate. The hard particle will minimize the matrix from the shear stresses [10]. Moreover, when the hardness increases, it tends to change the material property from ductile to brittle. If the material is brittle, it will reduce the absorbed energy during fracture [11].

3.5.3 Density and Porosity

![Figure 7](image)

**Figure 7.** (a) Density and (b) Porosity of Mechanical properties of Mg-Al-5Ti-B reinforced 0.20 Vf-% nano Al₂O₃ composites.

Density test results using the Archimedes principle obtained the actual density. The results of the actual density of the entire samples are compared with the theoretical density obtained from the calculation. From the results of density testing, the porosity percentage can be obtained. According to Figure 7, all of the stirred casting samples showed an actual density value much lower than the theoretical density and pure magnesium density. The addition of nano Al₂O₃ 0.25 Vf-% has the largest gap value between actual density and theoretical density, as well as the porosity had the largest number on that composition. It can be caused by the decrease of wetting effect as the increase of reinforcing particle’s amount, in addition to the tendency of agglomeration that causes the higher value of porosity [12].

4. Conclusion

The stir cast casting method may be used to fabricate Mg-Al-5Ti-B composite of the nano-Al₂O₃ particle. The addition of nano-Al₂O₃ can increase the UTS and elongation value at 0.20 Vf-% specifically, reduce the impact value, increase the hardness, decrease the wear rate, and increase the density of the material. The addition of 10%wt Al-5Ti-B’s aim to refine the material’s grain by forming initial nucleation, so that solidification occurs faster and is able to increase the material’s strength. The result of the microstructure shows the presence of MgO, MgAl₂O₄, Al₁₂Mg₁₇, and B₂O₃ phase.

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