Microstructure and mechanical properties of magnesium Si₃N₄ reinforced composite fabricated by stir casting method

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Abstract. Currently, the development of materials to improve the efficiency of fuel usage is increasingly carried out, one of which is a matrix composite. The stages of making composites in this study started from the preparation of magnesium matrix and Si₃N₄ reinforcement to casting with a stirring casting method. The addition of Si₃N₄ reinforce was carried out by varying the volume fraction by 2 vf-%, 4 vf-%, 6 vf-%, and 8 vf-% which was then characterized by metallographic testing, SEM-EDS, tensile testing, hardness, impact, wear, density and porosity, and XRD. The results of this study showed an increase in mechanical properties by adding Si₃N₄ as reinforcing particles. The magnesium composite produced different mechanical properties in each variation of the addition of the reinforce. The best mechanical properties resulted from the addition of a reinforce is with a volume fraction of 8 vf-% which produced a hardness value of 94 HRH and a wear rate of 0.0045 mm³/m.

Keywords: Efficiency of fuels, matrix composite, Si₃N₄

1. Introduction
The number of vehicle fuel consumption in Indonesia continues to increase every year, therefore improvements need to be made so that the use of fuel becomes more efficient. That way, the costs incurred to buy fuel, and the use of natural resources to produce vehicle fuel can be reduced. This will have a significant impact, especially to the environment, because CO₂ gas emissions are comparable with fuel consumption [1]. Generally, parts of vehicles are made using aluminum because of their good strength. However, to reduce the mass of the vehicle, aluminum replacement materials are needed. Magnesium is considered as feasible to replace the role of aluminum as a base material for vehicle parts with consideration of its relatively light mass, abundance in nature, and easy fabrication process, so as to reduce costs [2]. However, pure magnesium does not have as much strength as aluminum, so engineering process is needed so that good mechanical strength can be achieved. Therefore, it is necessary to do the mixing of magnesium with the reinforcement by using the micro-sized silicon nitride (Si₃N₄) ceramic particles. Silicon nitride reinforcement has a good affinity with magnesium, excellent mechanical properties, good wear resistance, strength, and good toughness so that ceramic particles are considered to be attractive for fabrication of metal matrix composites [3].
2. Materials and method

2.1. Materials
Materials used in this composite fabrication were pure magnesium ingot, purchased from Xiamen ITG Group Corp. LTD, as the composite matrix, and commercial Si₃N₄ micro-particle in 2, 4, 6 and 8 vt-% variation as the reinforcing particle. Composite mass balance calculation was conducted to prepare the materials needed.

2.2. Fabrication of magnesium with Si₃N₄ micro-particle composite
For the preparation, the surfaces of furnace, mold, and crucible were coated by zircon and graphite compounded with thinner, followed by the cutting of magnesium ingot with bandsaw machine into small blocks, and afterward the blocks were washed and wiped with alcohol to clean inclusion on the ingot surface before the blocks were put into the furnace. Furthermore, the remaining gases in the furnace were emptied out using vacuum pump followed by given of cover gas flux with argon flowed continuously until the casting was finished. On the other hand, the micro particle reinforce Si₃N₄ were heated in the muffle furnace at 950 °C for 30 min as a pre-heating step to remove moisture. Pre-heated reinforce were later put into the furnace and then immediately stirred with metal rod stirrer for 2 min to homogenize the molten metal. The molten metal was then poured into the mold, followed by air cooling at room temperature [4].

2.3. Characterization
Several tests to characterize the chemical composition of elements for each sample of composite were carried out using Optical Emission Spectroscopy (OES) to determine the composition of magnesium ingot, and X-Ray Diffraction (XRD) to find out the compounds formed in the material according to the principle of the difference electrical voltage exists at the anode and cathode. Then, the microstructure was observed using Optical Microscope (OM) to define the composites microstructure, and Scanning Electron Microscope (SEM) testing, then followed by Energy Dispersive Spectroscopy (EDS) to predict the formed phase which can not be observed using OM, and also to determine the distribution of particles in composite. Mechanical properties of each sample of composite were determined using these following step, that is porosity and density testing using a digital machine based on ASTM 378-88 to determine actual density of the composite, tensile testing using GOTECH AL-7000 machine to determine the ultimate tensile strength (UTS), hardness testing through the Rockwell H method using ROCKY machine, impact testing with GOTECH machine to determine each composite toughness, and wear testing using pin-on-disc OGOSHI machine with 100 m sliding distance to determine wear rate on each sample of composite.

3. Results and discussion

3.1. OES testing
Based on the results shown in table 1, the percentage of magnesium in each variable of reinforcing is above 96 % which means that content of magnesium in composites are ideal because the percentage of magnesium are below 98 % [5]. Si₃N₄ is a compound and since the OES testing can only detect chemical elements therefore the Si₃N₄ compound cannot be identified. Ideally, composites only contain magnesium element without the presence of other elements.

However, the OES test results contained several additional elements in the material being tested. This was caused by the casting process of as-cast magnesium and magnesium composites, the condition of the crucible in the furnace and the crucible for pre-heating of Si₃N₄ reinforce was not completely clean, so that other elements were mixed into the matrix as inclusion.
Table 1. Chemical composition of magnesium composite.

| Element (%) | As-cast | 2 Si₃N₄ | 4 Si₃N₄ | 6 Si₃N₄ | 8 Si₃N₄ |
|-------------|--------|---------|---------|---------|---------|
| Mg          | >96.6  | >96.0   | >96.0   | >96.0   | >96.0   |
| Si          | 0.861  | 1.23    | 1.81    | >1.40   | 1.56    |
| Fe          | 0.0041 | 0.0046  | 0.0026  | 0.0040  | 0.0045  |
| Cu          | 0.00070| 0.00023 | 0.00019 | 0.00025 | 0.00016 |
| Mn          | 0.0073 | 0.0157  | 0.0096  | 0.0176  | 0.0097  |
| Cr          | 0.0022 | 0.0020  | 0.0014  | 0.0018  | 0.0018  |
| Ni          | <0.00040| <0.00040| <0.00040| <0.00040| <0.00040|
| Zn          | 0.0152 | 0.0189  | 0.0194  | 0.0161  | 0.0153  |

Figure 1. Results of XRD testing of Mg/8 vf-% Si₃N₄ composite.

3.2. XRD testing
Based on figure 1, it appears that at each peak point there is a magnesium phase. This indicates that magnesium as a matrix is the most dominant phase in magnesium composite samples. The Si₃N₄ phase is seen at almost every peak point. This shows the fairly even distribution of Si₃N₄ reinforcing particles in all parts of the pure magnesium matrix in the magnesium composite sample with Si₃N₄ reinforcement. In addition, there is a MgO phase formed, this is due to the characteristic of magnesium which is very reactive and easily reacts with oxygen to form MgO [6]. The presence of Si₃N₄ reinforcing particles in magnesium composites makes magnesium composites is better compared to the magnesium as-cast.

3.3. Microstructure
Based on the results of microstructure observations shown in figure 2, it shows that in the composition of the reinforcement of 2 %, visible brownish-white areas were identified as pure magnesium phase and also grayish-black grains scattered in the magnesium matrix area where the grains are known as the reinforcing phase, while the black grains that clump in one area are known as agglomeration [7].
Figure 2. Microstructure of magnesium composite with (a) 2 vf-%, (b) 4 vf-%, (c) 6 vf-% and (d) 8 vf-% Si₃N₄ reinforced.

Then, the observation on the composition of the 4 % reinforcement shows visible blackish-gray areas that are lumpy and known as porosity. The observation of the composition of 6 % reinforcement obtained agglomeration of Si₃N₄ particles which is more than other microstructure compositions. Furthermore, the observation of the 8 % reinforcement composition shows that the reinforcing particles are dispersed equally in all area of the magnesium matrix, and only some small regions of porosity and agglomeration in the microstructure are observed.

3.4. SEM-EDS
SEM-EDS testing only performed at 8 % reinforcement composition. In this composition, the resulting composite is the most optimal based on tensile testing, so it is considered as the most representative for SEM testing. The results of this test are shown in images with a magnification of 250 x as shown in figure 3.

Then, from the EDS data shown in table 2, the distribution of N elements in the composite matrix tends to be uniform. However, at several points, namely at points 13, 14, 15 and 22, there is a relatively large content of Si element compared to other points, but the difference is not too significant. In addition, it can be seen that all selected points indicate a high O content, which indicates the presence of MgO compounds which are the rust products or oxidation products. The large amount of MgO compounds is formed due to the very reactive and easily oxidized of magnesium. In addition, the presence of C element is also seen at fairly low levels at all test points [6].
Figure 3. Results of SEM-EDS analysis of Mg/8 vf-% Si₃N₄ composite.

Table 2. Results of EDS testing of Mg/8 vf-% Si₃N₄ composite.

| Point | C (%) | N (%) | O (%) | Mg (%) | Si (%) | Possible phase formed          |
|-------|-------|-------|-------|--------|--------|--------------------------------|
| 11    | 1.36  | 0.70  | 39.62 | 55.75  | 2.57   | MgO, Mg₃Si                   |
| 12    | 1.87  | 0.00  | 39.30 | 57.62  | 1.20   | MgO, SiO₂                    |
| 14    | 0.88  | 1.71  | 41.98 | 44.03  | 11.41  | MgO, SiO₂, Mg-Si₃N₄          |
| 15    | 1.45  | 1.63  | 41.84 | 43.47  | 11.61  | MgO, Mg₂Si, Mg-Si₃N₄         |
| 16    | 1.96  | 0.33  | 40.27 | 52.36  | 5.09   | MgO                          |
| 17    | 1.62  | 1.29  | 40.62 | 49.30  | 7.17   | MgO, Mg-Si₃N₄                |
| 18    | 2.15  | 0.01  | 39.54 | 55.87  | 2.43   | MgO, SiO₂                    |
| 19    | 1.86  | 0.20  | 39.17 | 57.76  | 1.01   | MgO, SiO₂                    |
| 20    | 1.46  | 1.92  | 41.01 | 46.45  | 9.16   | MgO, Mg-Si₃N₄                |
| 21    | 1.40  | 1.98  | 40.96 | 46.67  | 8.99   | MgO, Mg-Si₃N₄                |
| 22    | 1.18  | 1.94  | 42.19 | 41.82  | 12.87  | MgO, Mg-Si₃N₄                |

Table 3. Result of density and porosity testing of Mg/8 vf-% Si₃N₄ composite.

| vf-% Mg (%) | vf-% Si₃N₄ (%) | Theoretical density (g/cm³) | Actual density (g/cm³) | Porosity (%) |
|-------------|----------------|-----------------------------|------------------------|--------------|
| 100         | 0              | 1.74                        | 1.701                  | 2.251        |
| 98          | 2              | 1.7686                      | 1.767                  | 0.109        |
| 96          | 4              | 1.7972                      | 1.772                  | 1.424        |
| 94          | 6              | 1.8258                      | 1.783                  | 2.337        |
| 92          | 8              | 1.8544                      | 1.844                  | 0.562        |

3.5. Density and porosity
The formed porosity in each sample according to the Si₃N₄ reinforce composition variable can be calculated by referring to ASTM 378-88. The results of these calculations can be seen in table 3, where the 6 % reinforcement composition is the variable that has the highest porosity percentage, which is 2.333 %. 
Based on the comparison results as in table 3, it can be seen that the actual density value of each Si₃N₄ reinforce composition variable is always smaller than the theoretical density value. This is caused by the formed porosity.

3.6. Tensile and elongation
Based on figure 4a, it is seen that the addition of Si₃N₄ reinforcement can increase the maximum tensile test value compared to magnesium metal without additional reinforcement. This is caused by increased material resistance to the occurrence of deformation which is the impact of an increase in dislocation density on the composite [8]. The strengthening mechanism occurs through the formation of the interface phase between the magnesium matrix and the Si₃N₄ reinforce [9].

On the other hand, the value of maximum tensile strength in the composition of reinforcement 4 % has decreased, even lower than the magnesium metal without reinforcement due to agglomeration that occurs. It can be seen in figure 4b, that in addition to get the maximum tensile test value, tensile testing can also provide information about the percent elongation that occurs in the composite after tensile testing. The percentage of elongation is inversely proportional to the material stiffness, as shown by the results of tensile testing conducted. It can be seen that the highest percentage of elongation is owned by the composition of Si₃N₄ reinforcement as much as 6 % with elongation percent of 17, and at the composition of reinforcement 8 % which has a maximum tensile value which is very high, with a magnitude of percent elongation of 7. Whereas, in the composition of the reinforcement of 2 %, the amount of percent elongation of 14 still tends to be high even though the value of maximum tensile strength is highest. This is caused by the lack of stress concentrations that are formed because the strain is spread evenly due to fine grains that well-occurred.

3.7. Hardness, wear rate and impact
Based on the hardness value obtained in figure 5a, it is seen that the highest hardness value of the composite is obtained from 8 % reinforce composition, which is 94 HRH. It is shown from the result in figure 5a that there is an increase in the hardness value of magnesium as-cast compared to magnesium composites with Si₃N₄ reinforce.

The more reinforcement particles will increase the hardness value of the composite. This is because the higher the level of Si₃N₄ reinforcement, the grain size in the matrix will be smaller due to obstruction of the growth of the magnesium matrix by reinforcing particles [10], which is followed by an increase in compressive resistance. In addition, the Si₃N₄ particles added to increase the area of the reinforcement and then the particles block the dislocation movement so that the hardness value increases and the material becomes more difficult to deform. Wear rate values in magnesium composites increased at 2 % composition and 6 % composition. This is because in the composition, magnesium composites have decreased the value of toughness so that the wear rate will increase. The increased wear rate is also caused by the agglomeration of the composition. Because the interface strength between the matrix and the agglomerated reinforce is weakened [11], so more volume of material is eroded when tested.

![Figure 4. Graphics of (a) tensile, and (b) elongation of Mg/Si₃N₄ composite.](image-url)
Reduction in wear rate occurs at 4 %, and the highest reduction at 8 % reinforce composition, which is 0.0045 mm³/m. This is because reinforcing particles contribute to increase the material hardness. The harder the material causes less abrasion [12]. Increasing the volume fraction of the reinforce can also increase more surface protection of the matrix when it comes in contact with other materials due to more interface between matrix and the reinforce so the strength of the interface will prevent the composite from peeling off due to other material friction [13]. Increasing the value of toughness in the Si₃N₄ reinforced magnesium composite sample reinforced evenly dispersed reinforcement in the matrix, and served as a load-bearing element, namely the occurrence of the load transfer process first through a reinforced reinforce, so that a larger load is needed to do deformation [14]. However, the impact price value at the composition of 6 vf-% the value obtained tends to decrease this is because the value of the porosity percentage at the composition is higher when compared to magnesium composites with a reinforcement composition of 4 vf-%, where porosity can reduce the toughness of the resulting composite sample.

4. Conclusion
Pure magnesium composite reinforced Si₃N₄ can be fabricated using the stir casting method. The actual density of magnesium composites has a smaller value than the theoretical density. This is influenced by the percentage of porosity formed in the sample, where the greater porosity percentage will produce a smaller actual density value when compared to the actual density value. The addition of Si₃N₄ particles to the magnesium composite will increase the hardness and impact value of the composite, but it will reduce the wear rate of composite. The maximum hardness value is in the composition of 8 vf-% Si₃N₄, which is 94 HRH, because the more reinforce is added to the composite, the more interfaces between
magnesium and the reinforcement are formed, so more strength is needed to deform the material. It will also increase the impact price of the composite. Then, the highest impact price was found in the composition of 8 v\text{f-\%} \text{Si}_3\text{N}_4, which was 0.12 Joules/mm\textsuperscript{2}. The even distribution of the Si\textsubscript{3}N\textsubscript{4} particles and the dispersion that occurs in the reinforcing particles plays a role in holding the load, so that the toughness of the composite will increase, whereas minimum wear rate is in the composition of 8 v\text{f-\%} \text{Si}_3\text{N}_4, which is equal to 0.0045 mm\textsuperscript{3}/m, because the harder the material, it will reduce the volume of abrasive material.

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