Article

Fabrication of metal matrix composites based on hydroxyapatite by self-high propagating temperatures synthesis (SHS)

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Abstract: The use of cow bones for biomaterial is still limited; accordingly, the cow bones waste has low economic value. Basically, a human's and a cow's bones are the same in terms of their forming compound. Aluminum (Al) has the potential to combine with hydroxyapatite (HAp) to make metal matrix composites (MMC) that have the potential for biomaterials. Compatible elements to be combined with Al and HAp are magnesium (Mg), titanium (Ti), and Copper (Cu), used self-high propagating temperatures synthesis (SHS). MMC can be processed to be a useful, solid product. Applying pressure to the SHS reaction and heating process may result in biomaterial composite product consisting of some matrix materials such as Al come from cans materials used in the experiment was HAp that was processed from cow bones calcination, added by can that contained aluminum and wetting agent, namely magnesium. The exothermic temperature was 800-900°C. The compaction process was done to allow materials to be bound. Based on the ASTM F138 standard for element of biomaterials, the porosity value was below 30% and hardness level above 40 HV. Cow bones and can-based composite sample with the composition of HAp-Al-Mg: 85%-10%-5% met the standard since the hardness value was: 73.3 HV with a porosity value of 29.88%.

Keywords: hydroxyapatite; beverage cans; metal matrix composites, self-propagating high temperatures synthesis and biomaterials

1. Introduction

The statistics organization in Indonesia (BPS) reported that the beef production reach ±524.109 tons per year. The ratio between the beef and the bone was 1: 2.74, meaning that ±140.136 tons of cow bone is potential for reprocessing [1-2]. The use of cow bones is still poor, in particular for the application of engineering; accordingly, the cow bone has low economic value. This phenomenon because of no appropriate processing methods for the utilization of bone material. Basically, the human bones and cow bones are same in terms of their forming compound. About 65% of the mineral component in bones is hydroxyapatite (HAp) [3-4]. Beverage can (BC) is one of the metal wastes containing about 95% aluminum (Al) and are potential for recycling. More than 75% of cans use series 3xxx Al as their basic materials [5]. BC that contains Al is potential to be combined with HAp materials. Compatible elements to be combined with Al-BC and HAp are magnesium (Mg), titanium (Ti), and copper (Cu). Using exothermic heating method by machine compaction, composite materials can be processed to be a useful, solid product. Through self-high propagating temperatures synthesis (SHS) with ideal variable, a metastable state and high purity of an element will be obtained [6]. The use of SHS is a suitable method for processing metal and non-metallic powders. Mechanism process of SHS based on combustion of exotherms that has a high purity of materials powder, to obtain a metastable phase in synthesis and simultaneous densification as well. Based on the heat

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released from the process reaction, it was able to regenerate itself. While the high temperature that is being produced is sufficient for the synthesis of the desired material product [7] Applying pressure to the exothermic reaction and heating process may result in biomaterial composite product consisting of some matrix materials such as Al-BC, HAp from cow bones, and coupling agent as the catalyst to create a bond between matrix and reinforcement [8-9]. The product is expected to be applicable for metal matrix composites (MMC) such as biomaterial components. This study primarily aimed to generate a biomaterial composite material from cow bone and soft drink can that meets ASTM F138, thus resulting in a strong biomaterial with low specific gravity.

2. Materials and Experimental Methods

The materials used in this study were composites that were based on MMC of BC and cow bones, shown in table 1. Materials was adjusted to the composition of the use of beverage can-reinforced by cow bone composite. The matrix was the cow bones obtained from the slaughter house. Aluminum powder comes from the milling process of cleaned beverage cans.

Table 1. Materials used in the experiment

Element	Materials used in the Experiment		
	Material form	Size	As
Beverage cans		0.3 x 1 cm	Matrix
cow bones		-170 #	Reinforcement
Mg		250 μm	Wettability

During the preparation process, the bones were soaked in acetone for two hours and were boiled for three times. During the boiling, the fats attached to the bones were eliminated. Then, the bones were calcinated within a muffle furnace at 850°C. Soft drink cans were cut into small pieces, and by using disk mill, they were made into powders in the size of -170#. Calcination was done to decompose collagen and other protein compounds. In order to make sure the HAp content, the cow bones undergo XRD test. After that, the cans containing aluminum element were prepared. Aluminum can was washed and cut into a size of 1x1 cm. The next step was the milling process using a disc mill for nine minutes with 20 seconds on-off time. The aluminum powder was screened until a size of -170# was obtained. HAp, Al-BC, and Mg were mixed using shaker mill for two hours. The mixed powder was then compacted by ±171 MPa. The sample was placed in a specific mold and put into a furnace with a temperature of 800-900°C to ease the contact of composite powder. The exothermic heating of SHS was done for two hours. The process of exothermic heating, followed by compaction is displayed in Figure 1.

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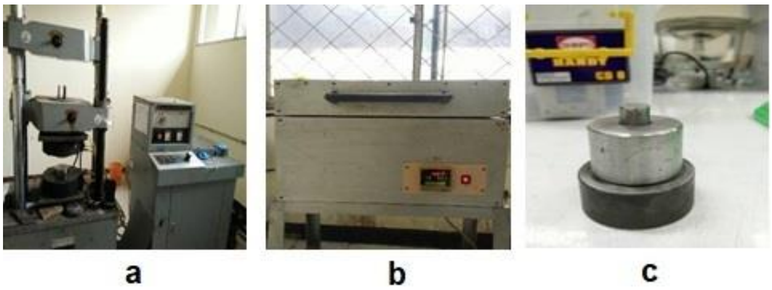

Figure 1. Equipment of SHS with exothermic pressing: a) Machine b) Muffle furnace c) Exothermic dies.

2.1 Characterization of Cow Bones and Beverage Cans

Porosity test were conducted to the composite's samples; the test was in accordance by standard: ASTM C 373 - 88. The sample was dried within an oven for 12 hours. After that, its dry weight was weighed. The sample was hung on the retort stand and was soaked in 100°C aquadest for 2 hours. After that, the sample was soaked in aquadest with room temperature for 24 hours. The wet weight was counted when the sample floated. The next step was weighing the saturated weight of the sample. The hardness test by micro vickers-hardness (HV), was applied in order to find out the materials ability regarding plastic deformation resistance against sudden loading. Scanning electron microscope (SEM) was used to determine the grain morphology and distribution of compound and phase generated by cow bones in HAp compound on Al, as well as the forms of phase from Mg as the wetting agent. Property investigation was done to determine mechanical properties, microstructure, and cow bones consolidation in the form of HAp on a can containing Al and Mg morphology. This investigation was based on the making of MMC from cow bones and beverage cans, combined with wetting agent, namely Mg. In order to find out the color and the morphology, EDS and XRD tests were carried out. The materials used in this experiment were HAp processed from cow bone calcination, added with cans containing aluminum. In order to help the bond between the phases, a wetting agent (i.e., magnesium) was added. Exothermic temperature between 800-900°C was applied using a muffle furnace, while the compaction was done using a pressing machine. The compaction process was applied to create contacts between cow bone of HAp as the matrix and cans, allowing the materials to be bound. Based on [7], the SHS process with a temperature below 1000°C cannot be done using the sintering method without compaction.

2.2 Measurement of Porosity and Density

The effect of adding Al beverage cans and magnesium on the porosity value of HAp is shown in fig 2. As shown in the table 2, the smallest porosity was found in the composition of 1% Mg (i.e., 21.31%). Whereas the largest porosity value was found in the composition of 12% Al can (i.e., 33.46%). The effect of adding Al and Mg is displayed in figure 2. Porosity decreases due to bonds between HAp and Al powder come from beverage cans; the pores were closed by the bonds. The effect of adding a wetting agent (i.e., magnesium) on the porosity value was shown in Figure 2b. The porosity value of the composition of 1% Mg was 21.33%, that of 3% Mg was 23.32%, and that of 5% Mg was 29.88%. The more the wetting agent is added, the higher the porosity value of the composite. This is consistent with previous study [10] stating that adding Mg to the composite may increase porosity, but the increase of Mg does not significantly enhance the porosity. Wetting agent refers to a material that damps the contact area of composite, allowing all elements to be attached to the matrix. The stronger the attachment between the reinforcement and the matrix, the lower the porosity of a composite. However, MgO has a high agglomeration property. Accordingly, although Mg strengthens the composite boned, Mg causes porosity value to be higher. MgO is formed due to the reaction between Mg and oxygen within the furnace. Besides, spinel that is formed in the composite can also increase the porosity value. Spinel can increase the porosity of a composite due to its property that is not capable of closing the gap between the composite's reinforcing particles [11].

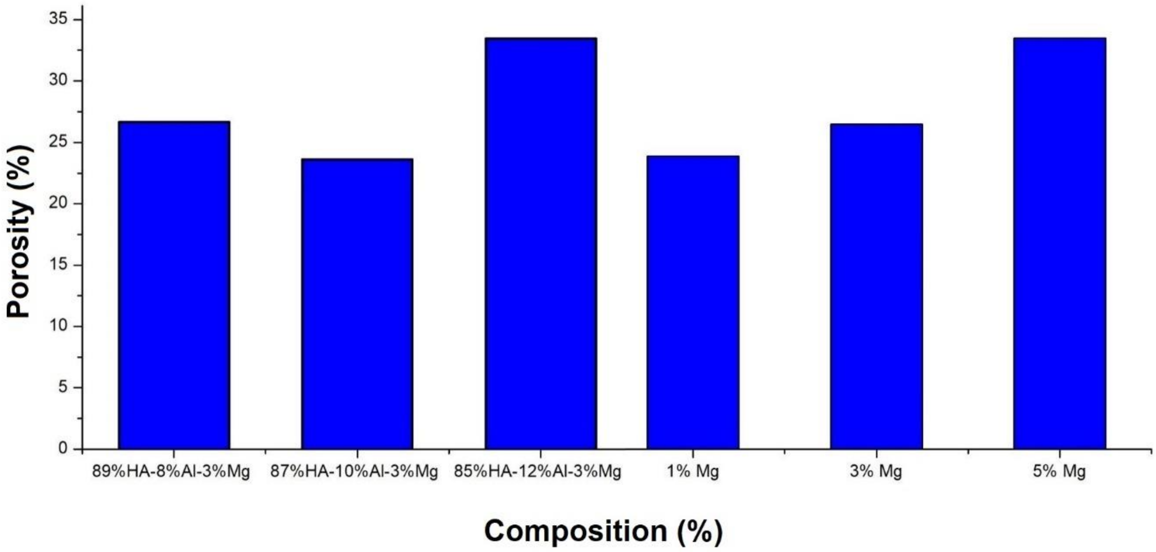

Figure 2. Effect of adding Al/Mg to the porosity value of diagram porosity.

3. Results and Discussions

3.1 Mechanical properties of MMC based on HAp

Hardness test was done using HV method. The test was done in some different points and results in data, as shown in table 2. The hardness value for sample with 8% Al, 10% Al, and 12% Al was 30.31 HV, 35.92 HV, and 8.49 HV, respectively. The highest hardness value was found in the composition of Al can 10%, that was 35.92 HV. By adding Al composition on HAp, the hardness value also increases. This shows that the interface bond occurs in the composite. Interface bond between Al/HAp occurs during the liquid-solid phase. In the temperature of 900°C, aluminum is in liquid phase while HAp is in solid phase.

Table 2. Mechanical properties value and porosity percentage

Composition	Hardness value (HV)	Average (HV)	Porosity (%)
87%HAp-10%Al-3%Mg	35.76		
	33.18	35.92	26.66
	38.83		
85%HAp-12%Al-3%Mg	13.52		
	5.65	8.49	23.62
	6.32		
89%HAp-8%Al-3%Mg	32.04		
	28.36	30.31	33.46
	30.54		
89%HAp-10%Al-1%Mg	26.22		
	19.5	21.04	21.31
	17.4		
85%HAp-10%Al-5%Mg	83.08		
	74.26	73.3	29.88
	62.56		

The lowest hardness level was found in the composition of Al 12%. The decrease in hardness value occurs because the contact area between aluminum and cow bones of HAp was not optimal, thus causing interface bounding not to occur. By applying pressure, the bounding between the elements may occur. The hardness value of the sample with 1% Mg, 3% Mg, and 5% Mg composition was 21.04 HV, 35.92 HV, and 73.3 HV, respectively. Adding Mg may increase the material's hardness value; this is proven by the result showing that the most significant hardness value was found in 5%. This indicates that the more Mg is added, the wetter the contact area between HAp/Al. However, due to many segregations occurred, the bond was not optimal. According to [10-11], wet surface of the contact area means that the surface stress between the surfaces become smaller. Thus, HAp and aluminum can have a robust bond.

3.2 Microstructures

Cow bones and Al-BC hydroxyapatite composite has rough morphology, as shown in Figure 3a. The surface with pores is indicated by black color, indicating that there is no light reflected by the materials, according to [12]. That part is the pores of the sample. The white part represents HAp, which can be seen from the rough and agglomerate structure. This agglomerate structure is found in hydroxyapatite made of calcination of the result of sintering [13].

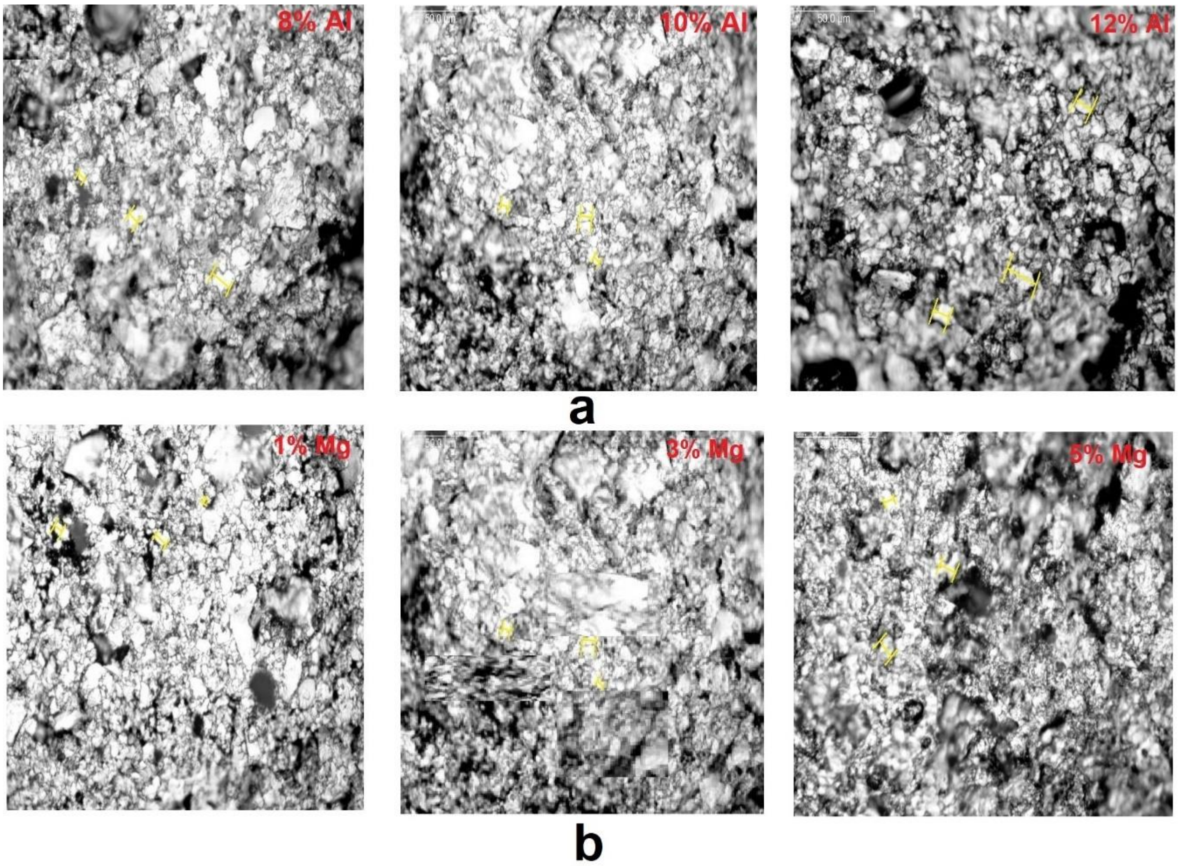

Figure 3. The microscope test result of the cow bone and can-based composite a) the effect of adding 8 – 12 % Al b) The effect of adding 1- 5 % Mg

Figure 3a, shown more aluminum cans addition leads to a decrease in composite porosity. Black color in the composition of 10% Al is fewer than that in 8% aluminum. Besides, the more the aluminum is added to HAp, the smoother the hydroxyapatite's surface. Most black colors were found in 12% aluminum. This is consistent with the porosity value. It was found that a composite of 12% aluminum has the highest porosity value. In Figure 3b, the most substantial porosity was found in 5% Mg. The number of porosities increases along with the increase of Mg in the composite. The composite's surface was agglomerate because of the property of MgO. In order to ensure the chemical bond formed in the composite, XRD test was done to see the composition of each sample, as shown in Figure 4.

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3.3 XRD Test

As shown in Figure 4. it could be concluded that adding aluminum-based cans to hydroxyapatite may increase the crystallinity of the HAp. The increase of crystallinity is shown based on the peak of the XRD graphic. A more regular peak in the XRD graphic indicates better material crystallinity. In composite 8% Al to 10%, the XRD peak was regular; however, in composite 12%, the decrease occurs. It could be concluded that when exceeding 10%, the crystallinity value of hydroxyapatite will decrease. There is an increase in the number of spinels ($MgAl_2O_4$) in the composite of 10% aluminum cans, compared to the composite of 8% aluminum cans. Spinel is a bond between Mg and Al that occurs in aluminum composite with Mg as the wetting agent. The stages of chemical reaction of the spinel formation occurring in the composite matrix ceramic formation process follow the equations below.

$$2Mg(l) + O_2 \rightarrow 2\,MgO(s) \quad (1)$$

$$4Al(l) + O_2 \rightarrow 2/3\,Al_2O_3(s) \quad (2)$$

$$Al_2O_3(s) + MgO(s) \rightarrow MgAl_2O_4 \quad (3)$$

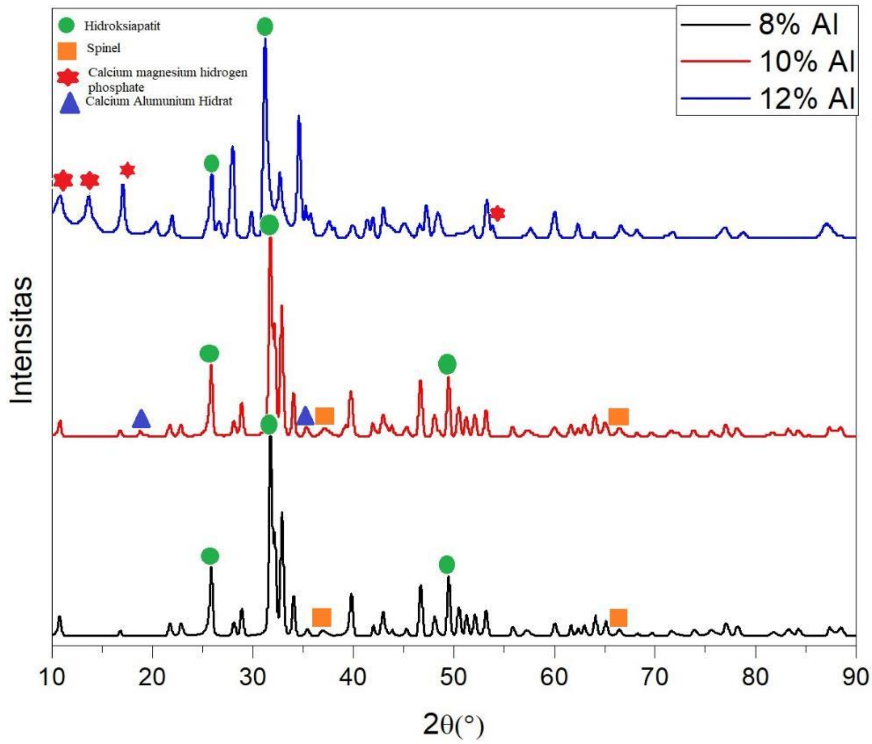

Figure 4. The XRD data on the effect of adding Al of MMC based on HAp.

Pure spinel itself has 15 GPa of hardness; accordingly, spinel may increase the hardness [14]. This is proven by the data on hardness value showing that the hardness value increase from 8% Al composite to 10% Al composite. While in 12% Al, spinel was not formed. This leads to no increase in the hardness value of composite with a composition of 12% aluminum. When adding Al 12%, calcium magnesium hydrogen phosphate was formed. This compound is a bond between magnesium and hydroxyapatite. This bond makes hydroxyapatite more agglomerated and increases porosity, then decreases its mechanical property. In general, magnesium will be more easily bound to aluminum sue to their similar property. However, this bond may also occur if the aluminum distribution is unequal, thus allowing Mg to more easily binds Ca to hydroxyapatite. Mg will be bound to hydroxyapatite following this reaction:

$$Mg + Ca_{10}(PO_4)_6(OH)_2 \rightarrow Ca_{10}\text{-}xMgx\,(PO_4)_5 \quad (4)$$

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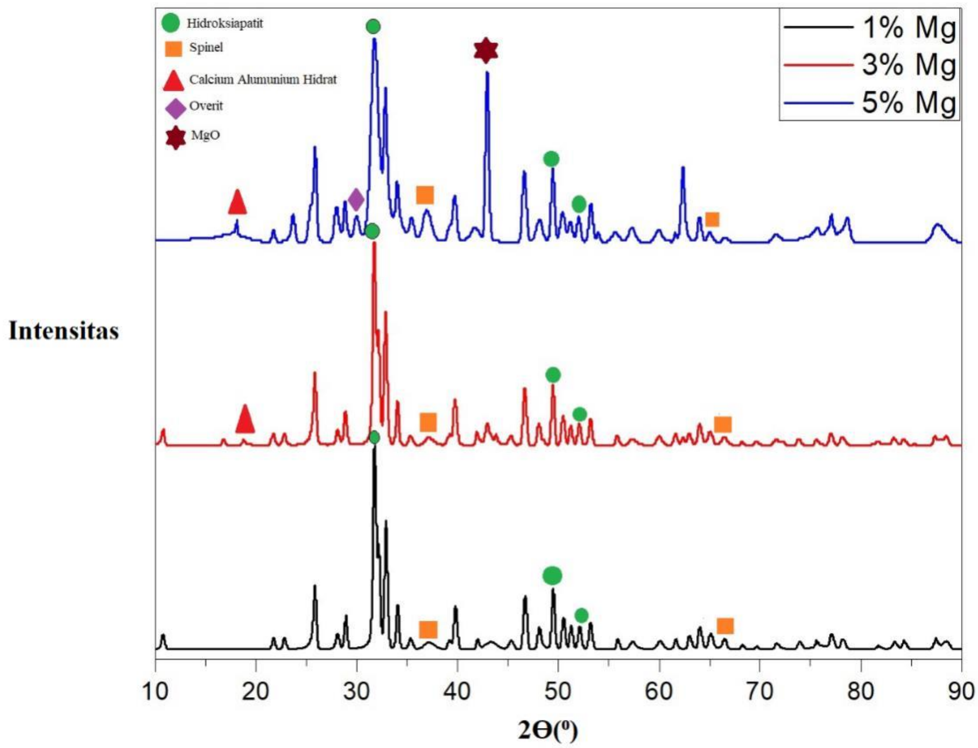

Figure 5. The XRD data on the effect of adding wetting agent (Mg) of MMC based on HAp

Calcium magnesium hydrogen phosphate has low mechanical properties, especially when the amount of calcium is larger than the magnesium. It is proven by the decrease in hardness value of Hap composite with 12% Al. Calcium aluminum hydrate is formed in composite with a composition of 10% Al. This proves that a bond between aluminum and calcium occurs in hydroxyapatite. This bond will be easily formed when aluminum is distributed evenly, allowing contact between aluminum and hydroxyapatite to occur.

Fig 5. shows data on XRD result of the hydroxyapatite-aluminum composite sample with different Mg compositions. The chemical bonds formed between HAp, aluminum, and magnesium increase when more magnesium is added. Based on the formed peak, it is found that the spinel's peak is increasingly higher. The hardness value also increases along with the increase of the spinel of the composite. This is proven by high hardness value on a 5% Mg sample that reached 73.3 HV. When adding 3% and 5% Mg, Calcium aluminum Hydrates is formed due to the increasing amount of wetting agent. Mg wetting agent manages to damp the interface area of hydroxyapatite and aluminum. The wet interface area is the contact angle between hydroxyapatite and aluminum. Smaller contact area allows the bond to occur easier when they are sintered in operational temperature. This is different from a 1% Mg sample, where it was the only spinel that was formed. In this sample, the number of Mg was very few, making aluminum to be bound directly with hydroxyapatite without help from Mg. The fewer the number of HAp bound to the can material, the smaller the hardness value. Compared to the 5% Mg sample, the 1% Mg sample's hardness value was only 21.04 HV. Overit ($H_9AlCaMgO_{13}P_2$) was formed in a composition of 5% Mg. It is formed based on a bond between aluminum, magnesium and hydroxyapatite. Besides, in a sample of 5% Mg, MgO was formed. In this sample, there were some Mg that were not bound to either Al/HAp. This unbound Mg reacted to the oxygen in the atmosphere. This reaction causes the Mg compound to change into MgO. An increase of porosity value occurs when the number of MgO of the composites increases. This sample was the one with the highest value of porosity (i.e., 29.8%).

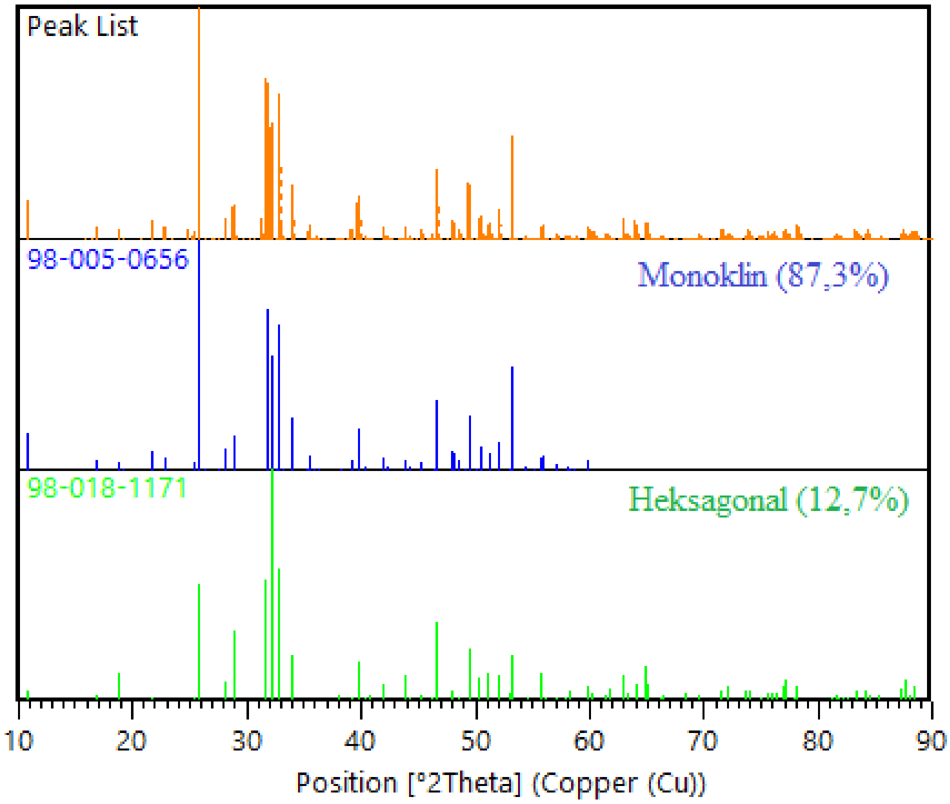

Figure 6. Peak list of sample HAp-Al-Mg 87%-10%-3%.

Based on high score plus data analysis, there was an increase in monoclinic hydroxyapatite crystal. As shown in figure 6, sample HAp-Al-Mg 87%-10%-3% had an increasing monoclinic crystal by 87.3%. The more the monoclinic HAp, the higher the stability of hydroxyapatite. Adding aluminum and wetting agent (Mg) may increase the stability of hydroxyapatite

3.4 Scanning electron microscope (SEM)

SEM was carried out to examine microstructure and element distribution of hydroxyapatite-aluminum composites. It was done to the sample with the highest and lowest hardness level, found that the sample with the highest hardness value was HAp-Al-Mg composition of 85%-10%-5%, while the lowest hardness value was HAp-Al-Mg composition of 85%-12%-3%. The microstructure of hydroxyapatite composite with the composition of HAp-Al-Mg 87%-12%-3% agglomerated. The agglomeration occurred because Mg was bound to HAp, forming calcium magnesium hydrogen phosphate compound. This calcium magnesium hydrogen phosphate had very agglomerate forms. It is usually used for bone glue. Mg, which supposed to only wet, was to matrix because its contact angle is smaller than that of Al. Besides, in this sample, many porosities were formed. Bonds between elements were not properly formed, resulting in many gaps. This is different from the sample with a composition of HAp-Al-Mg 85%-10%-5%, which had a smaller microstructure and was not agglomerate. As shown in Fig. 7 b. it can be seen that the composites bound to one another. In this sample, bond between Mg and hydroxyapatite did not occur. Accordingly, the agglomeration in hydroxyapatite is not as big as that in HAp-Al-Mg 85%-12%-3%. Based on the XRD data, it was found that the bonds that were formed were Mg-Al, Ca-Al, and Ca-Al-Mg. The rest of Mg were not bound to hydroxyapatite, but oxygen, resulting in MgO. Compared to Ha/Al/Mg 85%-12%-3% composition sample, the pores were fewer. Few pores in this sample are caused by Al reinforcement on hydroxyapatite, which was able to reduce porosity. The reinforced materials in the composite

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improve on property of the matrix if it has better properties than the matrix. Al has lower porosity value compared to hydroxyapatite, thus, Al can lower the porosity value.

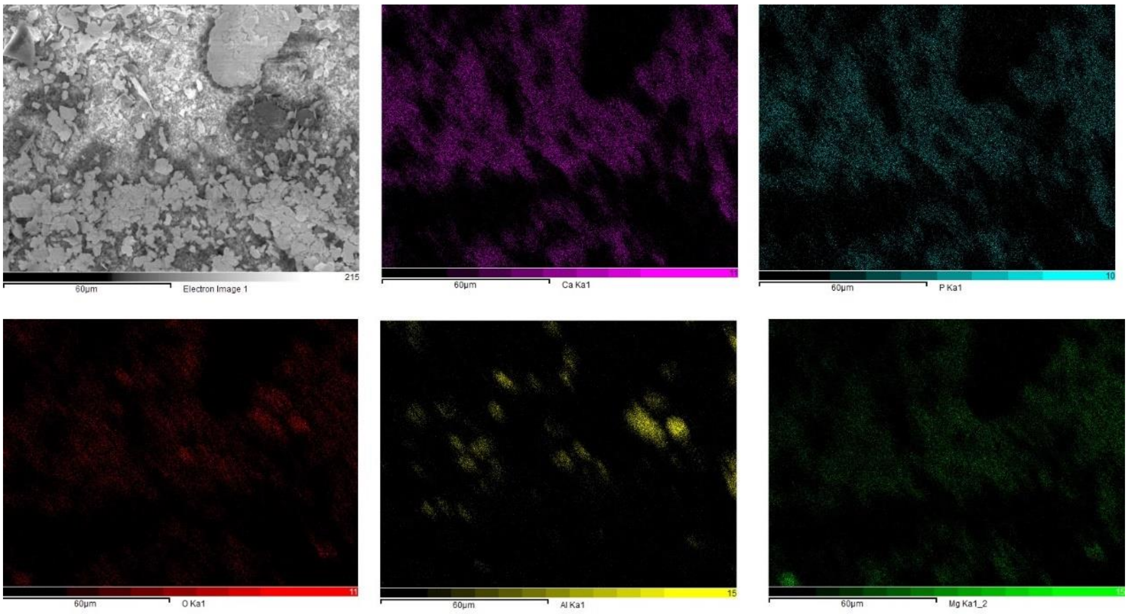

Figure 7 a. SEM-EDS Result of Hydroxyapatite composite with composition of HAp/Al/Mg 85%/12%/3%.

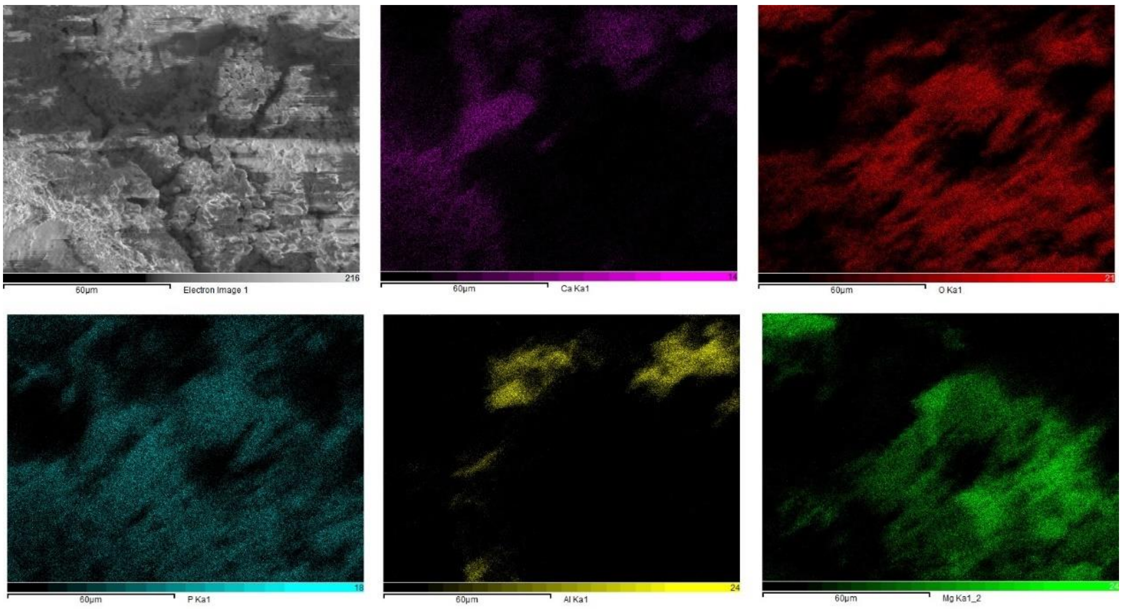

Figure 7 b. SEM-EDS result of Hydroxyapatite composite with composition of HAp-Al-Mg 85%-10%-5%.

3.5 Comparison of Microstructures

Based on the cortical bone standard with porosity value below 30% and hardness value above 40 HV [14]. Al-HAp composite with wetting agent Mg can be used as a cortical bone implant. All hydroxyapatite-aluminum composite had a porosity value of less than 30%, except the composition of HA-Al-Mg 85%-12%-3%. In other words, the porosity value of this composite exceeds the cortical bone standard. The hardness value of the cow bone-can composite that was higher than the cortical bone standard was found in the composition: HAp-Al-Mg:85%-10%-5%. As a recommendation, the composite with this composition (i.e., HAp-Al-Mg 85%-10%-5%) is applicable for cortical bone substitute. Cortical bone is also known as compact bone. Cortical bone is also known as a bone with porosity less than 30%. The average hardness value of cortical bone is 40.38 HV. The purpose of cortical bone includes protection, support, and storage of mineral.

Based on the application, as shown in figure 8, sample HAp-Al-Mg 85%-12%-3% had smaller grain size than sample HAp-Al-Mg 85%-10%-5% did. The diameter of the grain of the sample HAp-Al-Mg 85%-12%-3% was 785 nm -1500 nm, while that of sample HAp-Al-Mg 85%-10%-5% was 540 nm - 654 nm. This caused HAp-Al-Mg 85%-10%-5% to have higher hardness value, as shown in table 2, where the smaller the grain size, the higher the hardness value. Based on the cortical bone standard with porosity value below 30% and hardness value above 40 HV14. Al-HAp of MMC with wetting agent. Mg can be used as a cortical bone implant. All of HAp – Al had a porosity value of less than 30%, except the composition of HAp-Al-Mg 85%-12%-3%. In other words, the porosity value of this composite exceeds the cortical bone standard. The hardness value of the cow bone-can composite that was higher than the cortical bone standard was found in the composition: HAp-Al-Mg: 85%-10%-5%. As a recommendation, the composite with this composition (i.e., HAp-Al-Mg 85%-10%-5%) is applicable for cortical bone substitute.

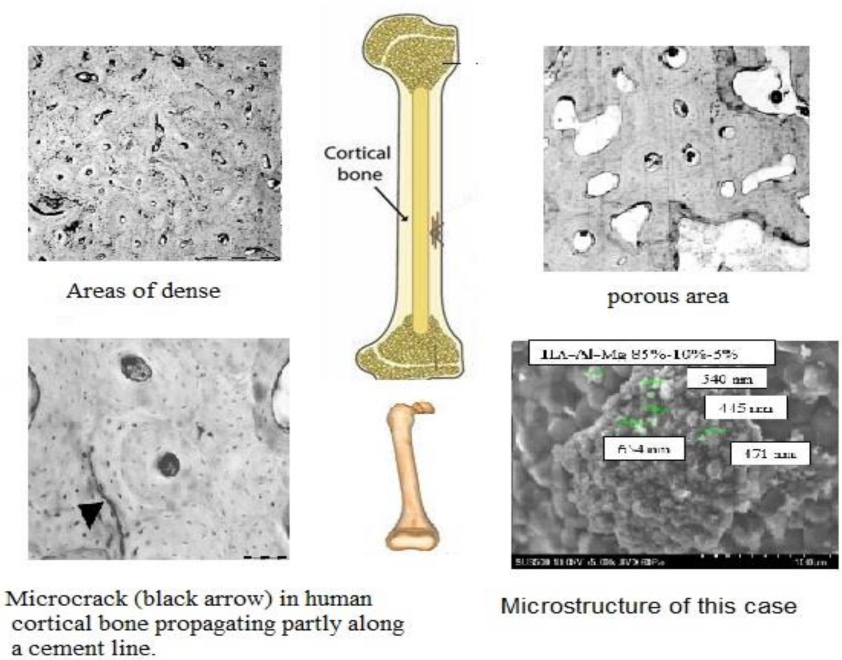

Figure 8. Forms and microstructure models of biomaterial applications

Cortical bone is also known as compact bone. Cortical bone is also known as a bone with porosity less than 30% [14]. This makes cortical bones very strong and dense. Its surface is smooth and white and is covered by a membrane called periosteum. The purpose of cortical bone includes protection, support, and storage of mineral. Since this tissue is robust, it protects vital organs and helps to support the body weight. Minerals required by the body, such as calcium, are also stored in the cortical bones until the body needs them. The average hardness value of cortical bone is 40.38 HV [15].

4. Conclusion

Adding powder of beverage can that contains of Al/HAp may reduce the porosity is in MMC based on hydroxyapatite. In contrast, adding a wetting agent (i.e., Mg) increases the porosity of HAp, although it is not significant. The lowest porosity value (21.31%) was found in the sample with a composition of HAp-Al-Mg 89%-10%-1%. Whereas the highest porosity (33.46%) value was found in the sample with a composition of HAp-Al-Mg 85%-12%-3%.

The wetting of magnesium on cow bone-based HAp/Al-B.C increase the hardness value of MMC. The highest hardness value (73.33 HV) was found in the composition of HAp-Al-Mg 85%-10%-5%; this sample is recommended for cortical bone application. The lowest hardness value (8.49 HV) was found in the composition of HAp-Al-Mg 85%-12%-3%.

This occurs because the wetting of Mg is suboptimal due to its low composition. Adding aluminum as the reinforcement and magnesium as a wetting agent for hydroxyapatite may form the following phase: spinel, calcium magnesium hydrogen phosphate, calcium aluminum hydrate, and overit. The agglomeration was found in sample HAp-Al-Mg 85%-12%-3% due to formation of calcium magnesium hydrogen phosphate.

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Conflicts of Interest: The authors declare no conflict of interest.

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