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To cite this article: Agus Pramono *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **532** 012004

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IOP Conf. Series: Materials Science and Engineering **532** (2019) 012004 doi:10.1088/1757-899X/532/1/012004

Calcination process on chanos chanos forsk (CCF) of milkfish bones to get Hydroxyapatite (HAp) as Composites Application

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Abstract. The material hydroxyapatite (HAp) from fish bone, $Ca_5(PO_4)_3(OH)_2$ used as a material of composite. HAp is an inorganic material that shows good biocompatibility for bone-connection material. It has excellent ability to form direct bonds with hard tissue in bone, when used as bone filler or as a ceramic coating on surgical implants. In this work, investigation focused on the suitability of fish bone material as a hydroxyapatite matrix with two additive elements ie magnesium (Mg), titanium (Ti) or copper (Cu) or another kind of coupling agent. Aluminium (Al) powder as a reinforcement in the composite materials. Investigation of morphological and structural properties of HAp samples derived from bone fish-chanos-chanos forsk (CCF) traced by microscope optical (M.O) to show the interconnected relative morphology grains to form complex compact matrix in hybrid composite materials. Analysis of sample elements using XRD to reveal the decomposition occurring at each calcination temperature. As well as a Finite Element Machine, type ANSYS R.18.2 trace simulation to ascertain how much actual temperature is occurring in the sample, it is necessary to trace the heat transformation that occurs within the HAp based composites of material. The test variable is the use of intermediate compositions, between the use of wetting agents between Mg-Cu, Mg-Ti or another combination of coupling agent. By high score software of XRD tracing to show how the hexagonal/monolith structures on HAp powder diffuses well against the wetting and reinforcing elements, so the process of the calcination will be applied for hybrid composite.

1. Introduction

Hydroxyapatite (HAp) is a crystalline molecule essentially composed of phosphorus and calcium, $Ca_5(PO_4)_3(OH)_2$ molecular formula. The 65% molecule consists of the mineral fraction present in the human bone. This material is also present in human tooth structure especially in dentine and enamel, this material is important in health world application. Bone of material has hydroxyapatite content, one of which is fish of bone, specially chanos chanos forsk (CCF). The Nutritional content of fish bone of CCF, based on laboratory test results found to contain calcium (Ca) as much as 4.7756% and phosphorus (P) as much as 1.3125%. Ca content in most milkfish found on the bone. Fish bone is one of the wastes that has not been utilized properly even though the CCF of milkfish bone contains of high calcium wastes are produced every day to reach 15-25 kg or about 5-12 tons per year. In Bone fish of CCF contains Ca 4%, P 3%, and 32% protein. Thus, the need for new product processing for

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waste making can be used optimally. One effort to utilize the waste by processing bone fish waste, but in the body of milkfish is suspected contain heavy metal copper (Cu).

This occurs from the shifting of Cu elements in the water content such as in the pond, the feasibility of inland ponds for milkfish culture can be determined the content of Cu in the body of milkfish ranging from <0.01 to 3.28 mg/kg, while the Cu content in pond water is <0.01 mg/l was undetectable [1-3]. Milkfish bones of CCF can be used as composite materials, milkfish bones such as: phosphorus, calcium and copper are elements that metallurgically can be combined with magnesium (Mg) as a wetting element that will provide an interface between the mixed material, made into a composite material with a material content of more than one type of matrix, this is referred to as hybrid-composite.

Currently, hybrid-composite material becomes the trend of future material technology because it can be applied to various types of components with high strength and mild density, so that the use of bone fish bone will lead to the eco-material that demands the development of material novelty without leaving the impact of pollution in the process of manufacture [3-4]. This research is an early synthesis of how the calcination process is done on the bone of CCF into hydroxyapatite, due to several advantages. The use of temperature following the ideal calcining temperature of bone of CCF between 600-700^{0}C. After becoming hydroxyapatite, it will be combined by metal material of using two type matrix or reinforcement for hybrid composites application.

2. Procedure Experimental

2.1 Heat Treatment on Milkfish bones of CCF

The initial stage was the washing of milkfish bone using water and soap to remove the fat and dirt that stick to the bones of milkfish, after a clean bone boiled until boiling for± 60 minutes. The next step is the heating process (calcination) to get hydroxyapatite, the heating was applied at a temperature of 500-700^{0}C. The reading scale inside furnace was 600^{0}C but outside the temperature of 700^{0}C by thermocouple reading scale, so it is necessary to search the actual temperature, using finite element method (FEM) by the new latest type 18.2 of ANSYS software. The heating process for obtaining hydroxyapatite shown in Fig. 1.

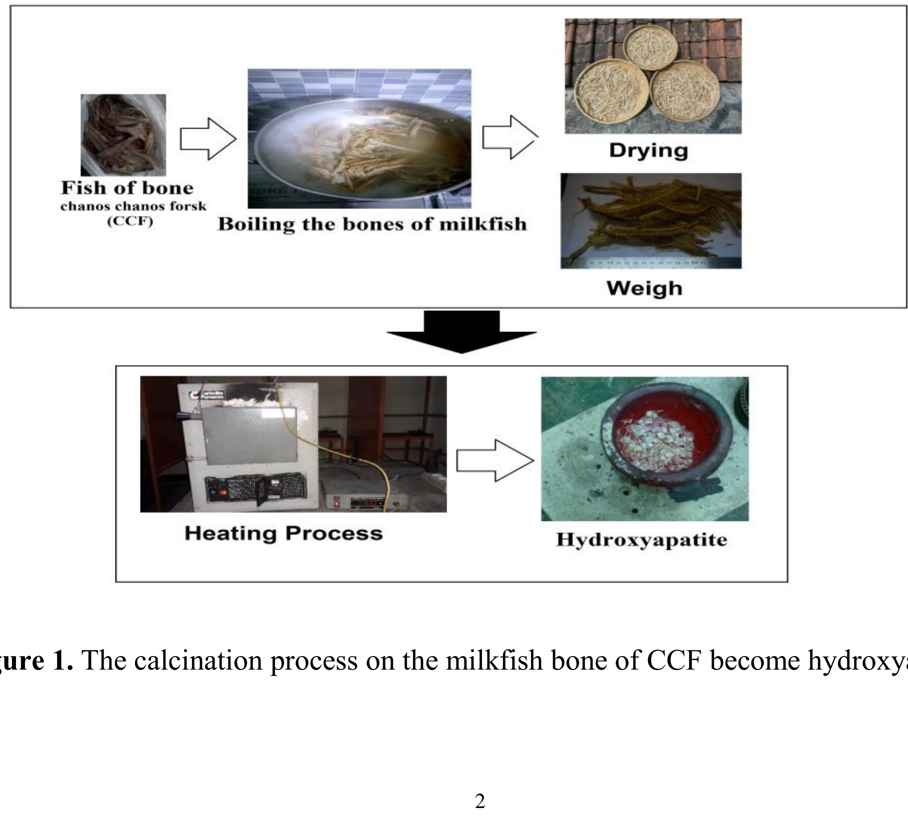


Figure 1. The calcination process on the milkfish bone of CCF become hydroxyapatite.

2.2 Characterization for obtaining hydroxyapatite of milkfish of bones (CCF)

The first test is the actual temperature accuracy tracking, this test used FEM software, to trace the actual temperature on the samples of milkfish bone (CCF). Temperatures need cross-check to get the actual temperature of the sample as a standard method of calculation of bone fish calcination, so that with the actual temperature standard can be used standard operates temperature. Micro-structural testing was performed to obtain an analysis of morphological changes in bone fish of CCF structure as well as bone defects such as porosity, segregation, or dirt on the bones of milkfish. This needs to be done to obtain an analysis related to the possibility of bone fish as a hydroxyapatite bone combined with a metal element as a composite base material. XRD testing is applied to obtain hydroxyapatite elements and possibly other luggage elements. using high score converters to determine the type of element or percentage of hydroxyapatite compound obtained. Among the tests will be applied a comprehensive analysis so that for the next stage can be obtained accurate hypothesis related to the application.

3. Hydroxyapatite as a Result Product

The heating process of bone fish of CCF calcination produces HAp. Formation of HAp depends on the suitability of temperature processes, on each heating from 1 to 5 hours resulted in different HAp in terms of physical and colour, at temperature 600^0C duration 2 hours produced HAp which still have black colour, suspected as carbon burning at CCF, evidenced in Fig. 2 in terms of colour and fig. 4 on microstructural observation results. Too longer the heating-up time, black colour turns brown until 4 hours. Within 5 hours produced bright of white colour without black or brown, this proves hydroxyapatite metamorphosed perfectly, but over than 5 hours, the overall bone of the fish was burning, this proves a transformation over than 5 hours, turning into total carbon. Changes of bone fish transformation presented in Fig. 2.

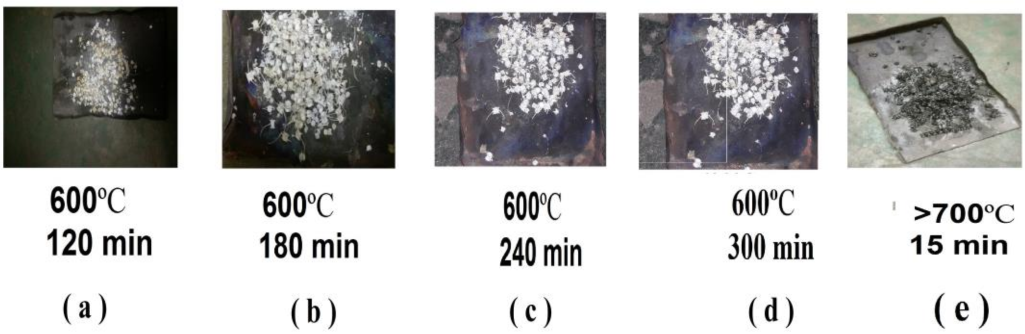
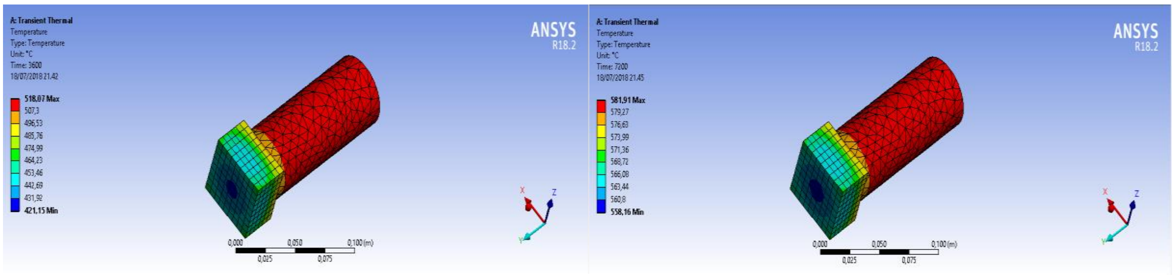


Figure 2. The hydroxyapatite colour change based on the duration of heating.

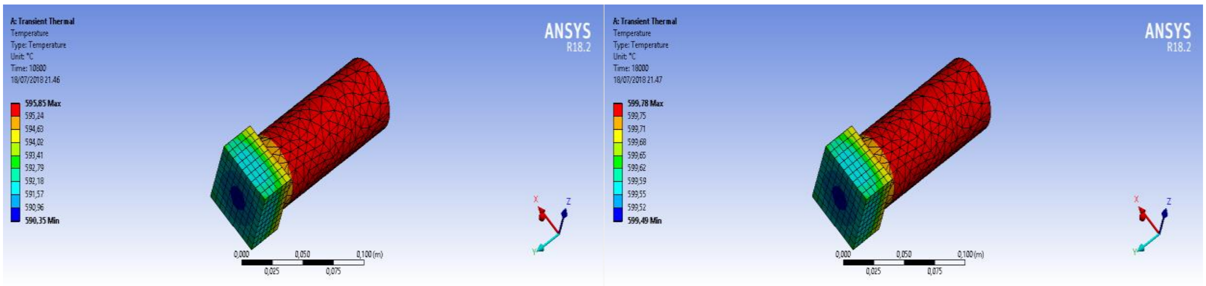
4. Result and Discussion

4.1 Simulation of samples Hydroxyapatite by FEM Ansys 18.2

Finite element machine (FEM) was applied to trace the temperature inside the furnace, CCF fish bone was inserted into the dies, and the temperature absorbed inside the CCF from the furnace to the inside of dies is presented in figure 3. In Figure 3 a. Temperature of 600^0C 1 hour indicates imperfect calcination, there was still black colour between the pieces of HAp in some parts, the temperature absorbed based on FEM still too low temperatures: 518^0C while at the base of the dies, the place where the bone was heated absorbed ±421-453^0C. Duration of 3 hours of heating is shown in Fig 3 b. Optimum temperature in the dies reaches 581^0C, at the bottom of the dies, where the CCF is placed, temperature are ±558-568^0C, if seen from fig 2 b. there is still black and brown colour indicating the hydroxyapatite is not perfect. Heating 4 hours fig 3 c. optimum temperature in the dies reaches 595^0C, on the bottom in dies where the CCF is placed, the temperature rises ±590-592^{0}C, seen fig. 2 c shown the black colour is not exist but brown colour still exist with a small amount. The carbon from the burning has changed to hydroxyapatite, brown colour is a transformation that indicates near perfect hydroxyapatite.



(a) **(b)**



(c) **(d)**

Figure 3. Heating of CCF into a 600^{0}C: (a) temperature for 2 hours (b). temperature for 3 hours c). temperature for 4 hours d). temperature for 5 hours.

Heating 5 hours in fig 3 d. the optimum temperature of the dies reaches 599^{0}C, at the bottom on the dies, where the CCF is placed, the temperature is 599^{0}C as well, this condition indicates that the heating is evenly distributed in all parts, seen from 2 d, no black and brown color. Complete combustion can affect the perfect transformation of hydroxyapatite.

4.2 Microstructures Analysis

The micro structure of the bone before heated was observed, in bones there was a grey colour that indicates the bone is still mushy, figure 4 a. CCF requires heating to transform into hydroxyapatite. Heating was try carried out at 600^{0}C for 1 hour. Figure 4 b. Heating for 1 hour there were some porosity in some connection bones, black whitish is the transformation from bone into CCF, up to 2 hours of warming 600^{0}C in the picture 4 c. Increased to the duration of 3 hours in figure 4.d some of the parts exposed to excessive heat into black carbon and transformation of white HAp is not perfect. On duration 4 hours 600^{0}C image 4 e. carbon is reduced and dispersed into freckles between the surface of the HAp structure. The 5-hour warming time of 600^{0}C is the ideal time, shown in Fig. 4 f. there is no carbon and the color turns brown and the presence of HAp is able to cover the porosity and blow holes into HAp structure grains.

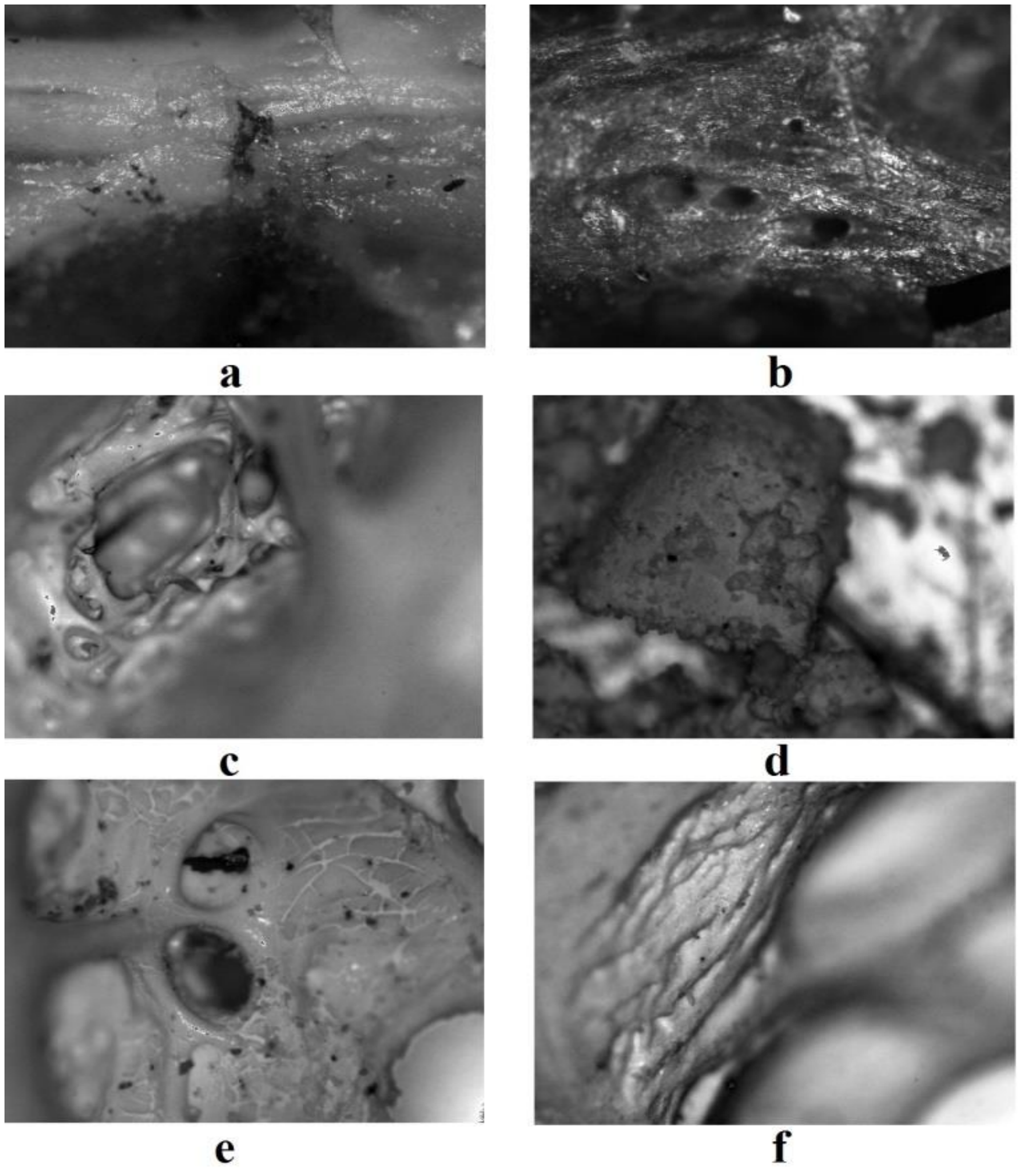
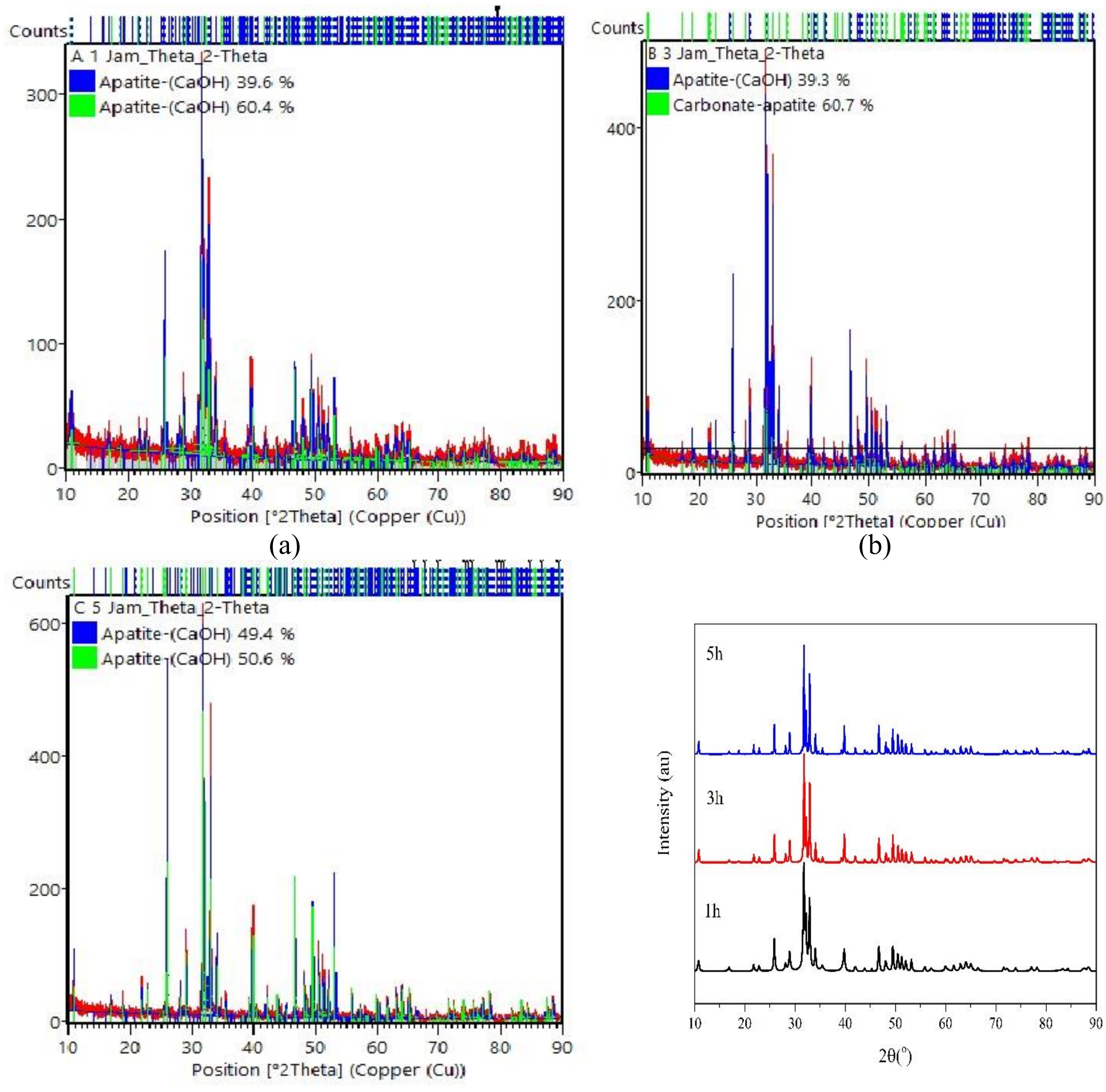


Figure 4. The Microstructure of CCF (a). CCF Non-heating (b). 600^0C 1-hour (c). 600^0C 2 hours (d). 600^0C 3 hours (e). 600^0C 4 hours (f). 600^0C 5 hours

4.3 Characterizations of XRD

XRD testing results prove that CCF contain of HAp, very dominant, accompanied by Ca and P. The HAp compound is $Ca_5(PO_4)3.OH_2$ [3] while Ca and P, are elements that have been bound in HAp. HAp can be CO_3 substituted properly with Tricalcium Phosphate (TCP) if the calcination temperature increases from 700-1000°C. The consolidated results show that the extracted HAp powder shows a crystallinity between 50 to 70% corresponding to the high palladium HAp phase crystallinity [5]. As in some other metal content such as Copper (Cu) or Lead (Pb) is the result of the absorption of the water environment where the milkfish live, such as the concentration of Pb in milkfish because in water there is a concentration of Pb [6]. Cu and Pb in fish bone tissue will interfere with integration with other metal elements in the composition, because it will make the segregation defect, so that the element is avoided in composite integration. The results of XRD will be recommended for hybrid composite with Al as a reinforcement, magnesium and titanium as a wetting agent and HAp as matrix.

The process to be used is Self-Propagating high temperature synthesis (SHS), with the help of pressure as an additional procedure [7]. Calcination of milkfish bones for 1 hour produced HAp as much as 39.6% HAp of monolith structure and 60.4% of HAp hexagonal structure, shown fig 5. a. In calcination, 3 hours in fig 5 b. resulted HAp of monolith structured as much as 39.3%, but remaining of 60.7% was dominated by carbonate. While 5 hour calcination of milkfish bones produces 49.4% HAp of monolithic structure and 50.6% HAp hexagonal structure presented in fig 5 c.



(c) (d)

Figure 5. Results of XRD calcination of CCF heating 600^0C (a) during 1 hour (b) during 3 hour (c) during 5 hours (d) Result of XRD analysis using high scores to obtain HAp of monolith structure.

The structure of HAP monolith structured is easier to react with metal elements as composite materials, compared to the hexagonal HAp of structure. Whereas carbonates are more likely to form fragility in composite materials. Calcination of 1 hour and 3 hours have not produced an optimal monolith structure compared to 5 hours calcination. The calcination process of milkfish bone during 5 hours produced a monolithic HAp structure that easily reacts with metal compounds as composite base material. Based on microstructural point of view, structural HAp contains calcium phosphate compounds, with characteristics similar to needle-shaped ceramics with angstrom size. this structure is very suitable to be used as matrix on concentrate of composite material [8]. Figure 6 shown data of XRD by high score software processing, milkfish CCF of bone structure presents the percentage of different elements, depending on the environment and the initial synthesis process. The black color from peak, indicated the bone of CCF was not produce the dominant HAp, the lack of heating time (1-hour calcination) makes the heat insufficient for the process of monolith structure collision, at the red peak, 3 hours warming of the HAp partially becomes carbonate. lack of heating time HAp is transformed into carbon which tends to be detrimental as an element. 5 hours is enough time to transform into a monolith HAp. This monolith structure can be used as the basis for composite formation.

5. Conclusions

Hydroxyapatite (HAp) is a crystalline molecule essentially composed of phosphorus and calcium, $Ca_5(PO_4)3OH_2$ molecular formula. The 65% molecule consists of the mineral fraction present in the human bone. The heating process (calcination) to get hydroxyapatite, the heating was applied at a temperature of 500-700^{0}C. The reading scale inside furnace was 600^{0}C but outside the temperature of 700^{0}C by thermocouple reading scale. The heating process of bone fish calcination produces hydroxyapatite (HAp), formation of HAp depends on the suitability of temperature processes, on each heating from 1 to 5 hours resulted in different HAp in terms of physical and colour. Five-hour heating time of 600^{0}C was ideal time, because there was no carbon and the colour turn brown and the presence of HAp was able to cover the porosity and blow holes into HAp structure grains. HAp product of CCF will be recommended for hybrid composite of ceramic matrix composites (CMC) with Al as a reinforcement, Mg/Cu as a wetting agent and HAp as matrix. The process to be used is Self-Propagating high temperature synthesis (SHS), With the help of pressure as an additional procedure, namely Exothermic Pressing (EP).

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