

SYNTHESIS AND CHARACTERIZATION OF HYDROXYAPATITE LAYER ON COBALT ALLOYS THROUGH DIP COATING METHOD AS A PROSTHETIC BONE IMPLANT CANDIDATE

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This research aims to determine the effect of dip coating process parameter, which are the concentration of the suspension, withdrawal speed and sintering temperature on the crystallinity, surface morphology, shear strength and the thickness of hydroxyapatite (HA) coating on cobalt alloys substrate as a prosthetic bone implant material candidate. The coating is done at 3 different concentrations of HA suspension: 0.02M, 0.04M and 0.06M by varying the speed of the withdrawal of 0.120; 0.198; and 0.266 mm/s followed sintering at temperature of 550°C with a holding time of 10 minutes. XRD test results showed that all concentrations formed the HA layer with hexagonal crystal structure as indicated by the appearance of the three highest peaks in the diffraction angle in $2\theta = 25.9316^\circ$; 31.8858° and 32.3164° the highest peak occurs at $2\theta = 31.8858^\circ$. HA layer crystallinity higher than nano HA powder because of the influence of the sintering temperature. SEM results showed that the HA layer formed not cover the entire surface of cobalt alloy substrate. The higher of the HA suspense concentration and the withdrawal speed will makes the thicker of the HA layer and the greater of the shear strength. Based on the thickness value of the layers so the proper sample for prosthetic bone implant applications is sample with concentration 0.06M with withdrawal speeds of 0.120 mm/s, 0.198 mm/s and 0.266 mm/s.

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1. Introduction

A joint replacement is necessary when the natural joint is damaged either by trauma or disease, thus requiring a bone implant prosthesis (permanent bone implant). Knee and hip joints are generally replaced when the articular cartilage between the joint surfaces thins that cause's joint gap (loosening) which lead to discomfort and pain for the patient [1]. Loosening the failure mechanisms in joint replacement due to the use of bone cement from cemented implants, this phenomenon is called aseptic loosening [2]. Bone cement (PMMA) has a lower modulus than bone as to reduce the pressure on the bone. Cement can also act as an absorbent layer between the bones elastic and rigid implants [3]. On the other hand the use of bone cement during the exothermic reaction raises the temperature of the polymerization process 70-120°C that cause damage to surrounding bone cells. In addition, aseptic loosening is accelerated by the presence of residual monomers which can lead to bone destruction. During the insertion process, shrink cement and its reaction are giving rise to strain in the area between bone and cement [4]. Thus cemented implant failure rate was significantly higher than uncemented. Therefore, recent research tends to focus on the uncemented implant coating metal implants with HA [3].

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Various methods of HA coating on titanium alloy substrates has been carried out including the method of pulsed laser deposition (PLD) [5-11] and RF magnetron sputtered [1]. The resulting layer is a strong layer, adhesive nature, pure, high crystallinity and breakage between the layers. However, both the coating method is complex and expensive. Another method is the electrochemical deposition [12] and biomimetic [13] it's kind of simple method but the resulting layer of amorphous HA, HA lattice parameter change and the resulting layer thickness of the order of 5-10 μ m.

In addition to the methods mentioned above there is a very simple method of coating the dip coating (coating with withdrawal). Dip coating method Si-HA on titanium alloy substrates has been carried out by Hijon et al [14]. In the dip coating method that forms a thin layer quality depends on the concentration of the suspension, the speed of withdrawal and the sintering process after coating. The concentration of the suspension affects the thickness and homogeneity of the resulting thin film. The lower the concentration the thinner the layer is generated and the stronger the adhesion between the coating material to the substrate [14, 15].

In addition to titanium alloys, other bone implant material is a cobalt alloy. Cobalt alloys have mechanical properties (elongation and fatigue strength) is higher than the tensile strength titanium alloy and titanium alloy equaling [16,17]. Potential cobalt alloys have been investigated Shamsul et al. [18,19] to synthesize Cobalt Implants Composite (CIC) which is a composite between cobalt alloy with HA via powder metallurgy method. On the composition of 5% HA, produced better properties when compared with other variations of composition (0-20%). In this composition of 5% HA resulting compressive strength (compressive strength) of 150 MPa that qualify as bone implant materials. Cytotoxicity assay with HA composite cobalt alloys on fibroblast cells showed that the percentage of live cells ranged from 78.6-95.8%, this indicates that the composite alloy of cobalt-HA is non toxic [20].

Based on the study of several methods that have been described above by considering the economic aspects and the simplicity of the process so it is easy to be developed at the level of production in this study carried the HA coating on cobalt alloy substrate by dip coating method. This study was conducted to determine how the effect of dip coating process parameters (concentration of the suspension, the speed of withdrawal and the sintering temperature after the coating process) on the crystallinity, surface morphology, shear strength and thickness of the HA coating on cobalt alloy substrate.

2. Materials and methods

The research was carried out in 3 stages. Stage 1: Preparation of a cobalt alloy substrate. Stage 2: The process of coating via dip coating method with various concentrations of suspension HA and withdrawal speed. Stage 3: Treatment sintering at a temperature of 550⁰C for 10 minutes.

Stage 1. Preparation of a cobalt alloy substrate

Cobalt alloy substrate synthesized by fusion method using a tri-arc melting furnace at 200A with the current composition of 62.25% Co-31.5% Cr-5% Mo-0.5% Mn-0.5% Si-0.25% N adapted to the ASTM F75 (American Society for Testing and Materials F75) [21] continued the process of homogenization at a temperature of 1300⁰C for 2 hours. The materials used are powdered chromium [Cr (99+) - Merck], cobalt powder [Co (99+) - Sigma-Aldrich], molybdenum powder [(Mo (99+) - Merck], powdered manganese [Mn (99+) - Merck], silicon powder (Si - Merck) and powder Cr2N (Nilaco). then cut using a metal alloy wire cut with varying sizes of 0.5 mm x 0.8 mm with a thickness of 2-3 mm, rubbed with coarse 80 grit silicon, washed with distilled water and then soaked it in ethanol.

Stage 2. Coating process via dip coating method

HA suspension in ethanol made with various concentrations: 0.02M, 0.04M and 0.06M. Cobalt alloy substrate is dipped into a suspension of HA-ethanol at various concentrations mentioned above and soaked for 10 minutes, then withdrawn by varying the drawing speed $v_1 = 0,120\text{mm} / \text{s}$, $v_2 = 0,198\text{mm} / \text{s}$ and $v_3 = 0,266\text{mm} / \text{s}$. The withdrawal speed of movement of the

motor is generated by varying the voltage source, each respectively is 6V, 9V and 12 V. Successive samples are named A₁, A₂ and A₃ (for concentration 0,02M at v₁, v₂ and v₃), B₁, B₂ and B₃ (for concentration 0,04M at v₁, v₂ and v₃) and C₁, C₂ and C₃ (for concentrations 0,06M at v₁, v₂ and v₃). The coating process is done 2x withdrawal of up and down. Layers allowed to settle, then a layer of dried at room temperature.

Stage 3. Sintering process

The dried layers sample then sintered use a tube furnace STF & TZF Models at 550°C temperature with a holding time of 10 minutes, with an increase rate of 10 ° / min and the decrease rate at 5° / min, argon purged under vacuum conditions with a flow rate of 3l / min [14].

Characterization of Samples

Thin film samples were characterized crystal structure using X-ray diffractometer PANalytical X'Pert PRO and surface morphology using Scanning Electron Microscopy (SEM- Fei Inspect S50). Test XRD using CuK α source with wavelength = 1,54060Å, the angle = 5°-60°, step size 0,0170°, scan step time 135,2550s, operated at 40 kV and 30mA. SEM test performed at a voltage of 20 kV with WD = 15.2 to 15.7 mm. Shear strength test using Shimadzu Autograph AG-10TE.

3. Results and discussions

The crystal structure of the HA layer XRD test results are identified with reference ICDD 01-074-0565. XRD test results are presented in Figures 1, 2 and 3.

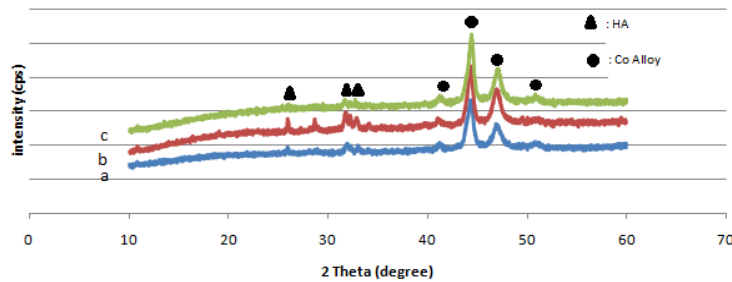


Fig 1. XRD Spectrum of sample 0.02 M concentrated, (a) A₁ (b) A₂ and (c) A₃

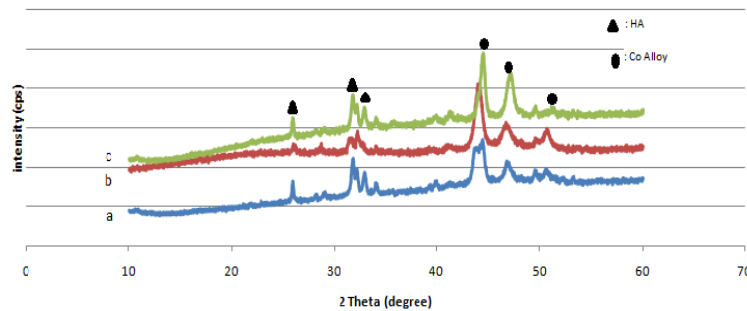


Fig 2. XRD Spectrum of sample 0.04 concentrated (a) B₁ (b) B₂ and (c) B₃

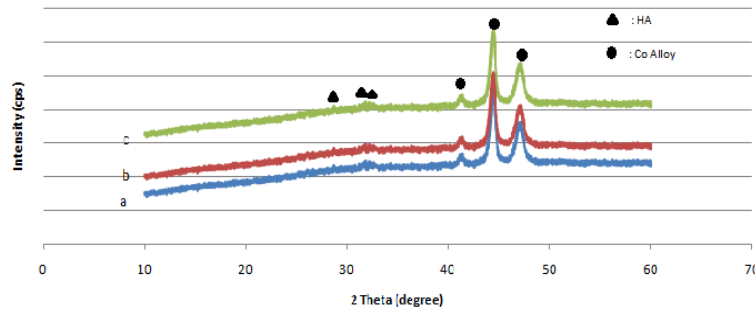


Fig 3. XRD Spectrum of Sample 0.06 M concentrated (a) C_1 (b) C_2 and (c) C_3

Based on the XRD results (Figure 1, 2 and 3) on the variation of the concentration of HA 0.02M, 0.04M and 0.06M have formed HA layer as indicated by the appearance of three peaks which occur at the highest diffraction angle 2θ around 25.9316° ; 31.8858° and 32.3164° with the highest intensity at $2\theta = 31.8858^\circ$. HA has a hexagonal crystal structure with lattice parameters $a = b = 6.8790\text{\AA}$ and $c = 9.4240\text{\AA}$. The highest intensity occurs at $2\theta = 31.8858^\circ$ for the entire sample are presented in Figure 4. When compared with the nano-HA powders without sinter ($I = 452\text{ cps}$), the HA layer sintering results have higher diffraction intensity. Diffraction intensity is correlated with the crystallinity of HA very influenced by the sintering process after coating. In the sintering process is carried out at a temperature of recrystallization HA causes vibrating atoms arrange themselves to form a more perfect crystal structure. So it can be said that the sintering process causes increased in crystallinity of HA. Except for the sample A_3 (0.02M concentration, velocity $v_3 = 0.266\text{ mm/s}$) the value of the highest diffraction intensity ($I = 349.65\text{ cps}$) is lower than the value of nano-HA intensity powder diffraction. It is alleged the sintering process on sample A_3 is less than perfect because of the position of the sample time of the end of the sintering process was a little more to get an argon flow, thus causing the atoms HA did not have enough opportunities to organize themselves into a perfect arrangement of atoms. In addition, due to the HA coating on very thin samples A_3 ($7.347\text{ }\mu\text{m}$) (Figure 9) causes the diffraction intensity of the cobalt alloy substrate is very high indicating that the cobalt alloy substrate dominates.

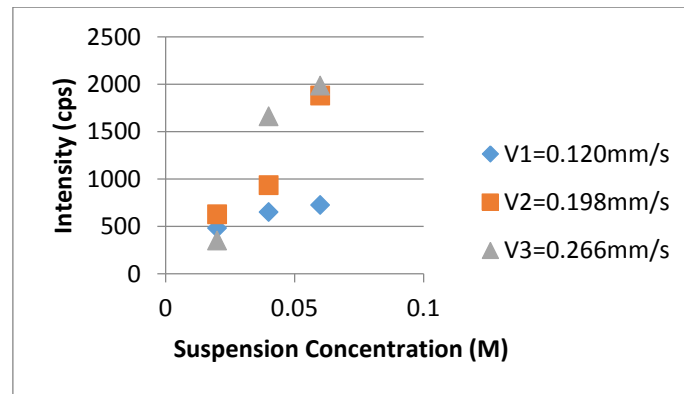


Fig 4. Intensity of Diffraction Vs Suspension Concentration at $2\theta = 31.8858^\circ$

In Figure 4 shows that the greater the concentration and withdrawal speed, the greater the intensity of diffraction. This is presumably the greater the concentration of HA and withdrawal speed the more the HA is attached to the substrate that causing the thick layer is formed. The thicker the HA layer, the presence of formed HA can be detected by XRD detector giving rise to higher diffraction intensity. Conversely, if a very thin layer of HA causes the presence of HA was not detected properly because it is dominated by cobalt alloy substrate.

The test results of SEM morphology of the surface layer of HA is presented in Figure 5 and Figure 6 while the cross-sectional morphology is presented in Fig. 7 and Fig. 8.

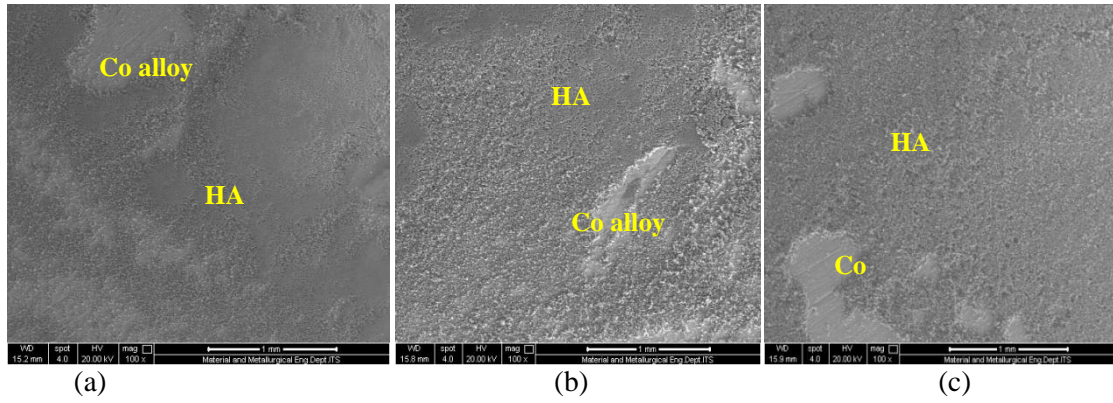


Fig 5. Surface Layer withdrawal HA at varying speeds with a fixed concentration of HA (0,06M), bright colors: Co alloy, dark color: HA layer (a) Samples C_1 , (b) sample C_2 , and (c) sample C_3

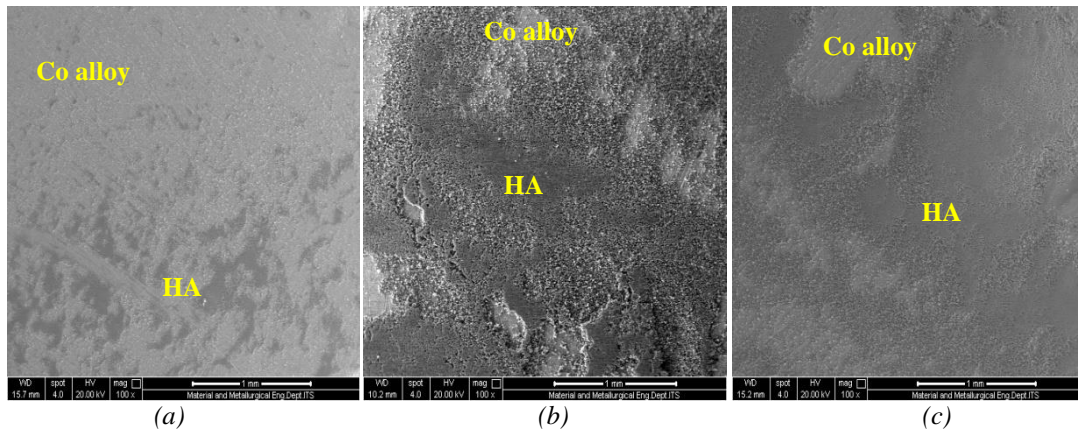


Fig. 6. Surface Coating HA at varying concentration with fixed withdrawal velocity ($v_1 = 0,120 \text{ mm/s}$), bright color: Co alloy, dark color: HA Layer (a) Sampel A_1 , (b) sampel B_1 dan (c) sampel C_1

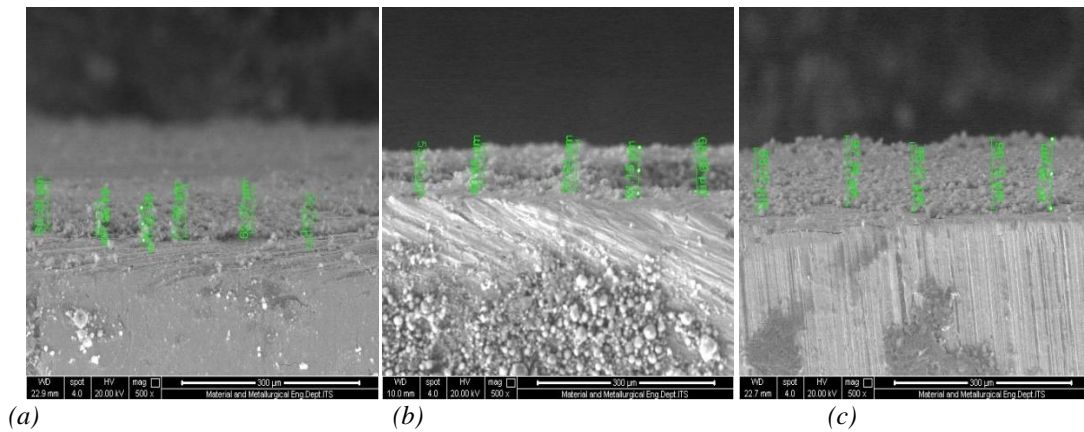


Figure 7. Cross-sectional HA coating at a withdrawal rate that varies with a fixed concentration of HA 0,06M; (a) C_1 , (b) C_2 and (c) C_3

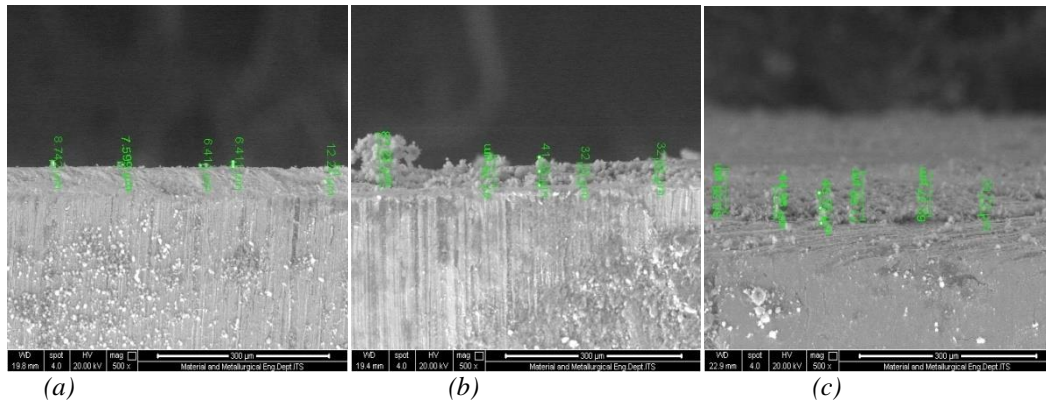


Fig. 8. Cross-sectional layer HA on variation concentration of HA suspension with fixed withdrawal speed $v_1=0,120\text{mm/s}$
(a) A_1 , (b) B_1 and (c) C_1

Based on cross-sectional morphology of the HA layer (Figures 7 and 8), can be calculated thickness of the entire sample are presented in Figure 9.

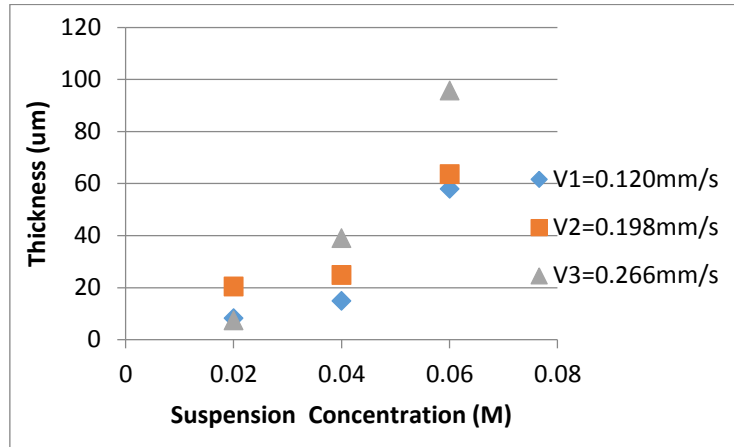


Fig. 9. The thickness of the layer of HA vs. HA concentration Suspension

Based on the SEM results (Figure 5 and 6) HA layer formed not cover the entire surface of the cobalt alloy substrate. Withdrawal speed variation (Figure 5) and the variation of the concentration of HA (Figure 6) did not produce significant differences on the surface of the HA layer formed. In Figure 5 and 6 it appears that the HA layer formed does not cover the entire surface of the substrate. In the withdrawal speed and the lower the concentration should result the average layer covering the surface due to the lower speed, the HA coating on the substrate so that the longer it lasts the expected layers formed more evenly. Unequal distribution of HA coating on cobalt alloy substrate either because of variation of concentration and withdrawal speed is affected by the drainage process (flow of solvent) and solvent evaporation process is less than perfect. It is presumed at low concentrations of ethanol drainage process is very fast so that sediment does not occur evenly throughout the surface of the substrate, whereas at high concentrations (0.06M) ethanol solvent quickly evaporates making the layers that form also does not cover the entire surface of the substrate.

Based on the thickness of the test (Figure 7, 8 and 9) it appears that the greater of the concentration of HA suspension and withdrawal speed, the greater of the resulting thickness. The greater of the concentration of HA and withdrawal speed means more HA that settles that the resulting layer thickness is also greater. Thickness obtained from the variation of the concentration and velocity ranges between 7.347-95.62 μm . Best Terms for medical applications in terms of aspects of the SBF solubility and does not cause clinical problems that layer with a thickness of

50-200 μm , [22]. Based on these criteria, the study sample that meets the standards of the aspects is the thickness of the sample C_1 , C_2 and C_3 . The results of shear test (shear strength) of the three samples are presented in Figure 10, respectively is 1.294 MPa, 1.783 MPa and 2.362 MPa. These results are still under research Bunyamin [23]. The difference is due to differences in substrate and sintering temperature. Substrate and sintering temperature greatly affect the adhesion layer. It is therefore advisable to increase the shear strength to increase the sintering temperature above 550°C .

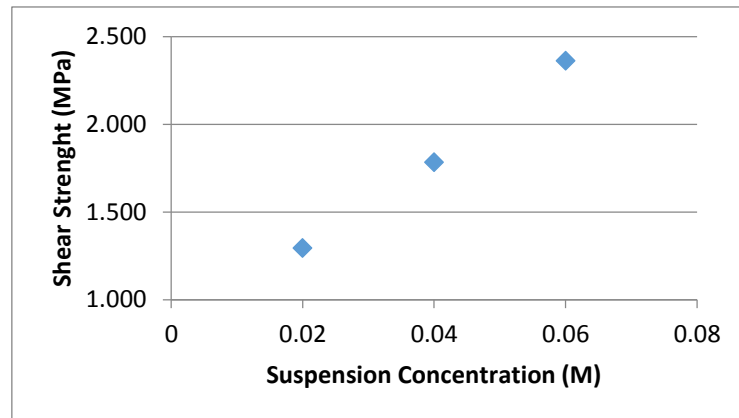


Fig. 10. Shear Strength of suspension concentration C_1 , C_2 and C_3

4. Conclusion

Has been successfully synthesized HA coating on a substrate with a cobalt alloy dip coating method. At concentrations 0.02M, 0.04M and 0.06M formed HA layer as indicated by the appearance of a third peak HA diffraction at angle $2\theta = 25.9316^\circ$; 31.8858° and 32.3164° the highest peak occurs at $2\theta = 31.8858^\circ$. HA coating of crystallinity higher than Nano-HA powders because of the influence of the sintering process. SEM results showed that the HA layer formed not cover the entire surface of the cobalt alloy substrate. HA suspension concentration and withdrawal speed affects the thickness of the HA coating. The higher concentration of HA suspension and withdrawal speed produces shear layer thickness and greater strength. Based on the value of the layer thickness of the resulting samples were eligible for the application of bone implant prosthesis (50-200 μm) are the sample C_1 , C_2 and C_3 consecutive samples with a concentration of 0.06M HA suspension on withdrawal speed 0.120mm/s, 0.198 mm/s and 0.266 mm/s.

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