

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 MCPM electrolyte based aqueous solution

4.1.1 As-deposited films

The current densities, which were applied to find an optimum condition, were -5 mA/cm^2 , -7 mA/cm^2 , -10 mA/cm^2 , -15 mA/cm^2 , and -20 mA/cm^2 for 3 minutes deposition time. In each condition, the film surface was different in which easily observed by naked eyes. Figure 4.1 shows optical micrographs of 50x magnified film surface.

From Figure 4.1 (a)-(e), We can see that film depositions were depended on their current density. At -5 mA/cm^2 (Figure 4.1(a)) and -7 mA/cm^2 (Figure 4.1(b)), films just started to deposit and did not completely covered titanium substrate surface. At -10 mA/cm^2 (Figure 4.1(c)), -15 mA/cm^2 (Figure 4.1 (d)), and -20 mA/cm^2 (Figure 4.1 (e)), films completely covered the titanium substrate. When we observed closer, it could be seen that the lower the current density was, the smaller round shape crystals formed, on the other hand, the higher the current density was, the larger needle-like shape crystals (Figure 4.1(e)) formed.

From films surface observed by an optical microscope, OM, it seemed that the current density of -10 mA/cm^2 was the best condition because its small crystals formed with uniform size and completely covered the surface of Ti substrate. So, this condition was selected to further study at the different deposition times (3 and 5 minutes).

For cross-section technique, the specimens were mounted in clear resin and left to be fixed in the polymerized resin, then polished by silicon carbide powder and followed by diamond pastes until the cross section the surface exposed. As a result, film

thickness of as-deposited films at 3 minutes and 5 minutes were able to be investigated by cross sectional technique as shown in Figure 4.2.

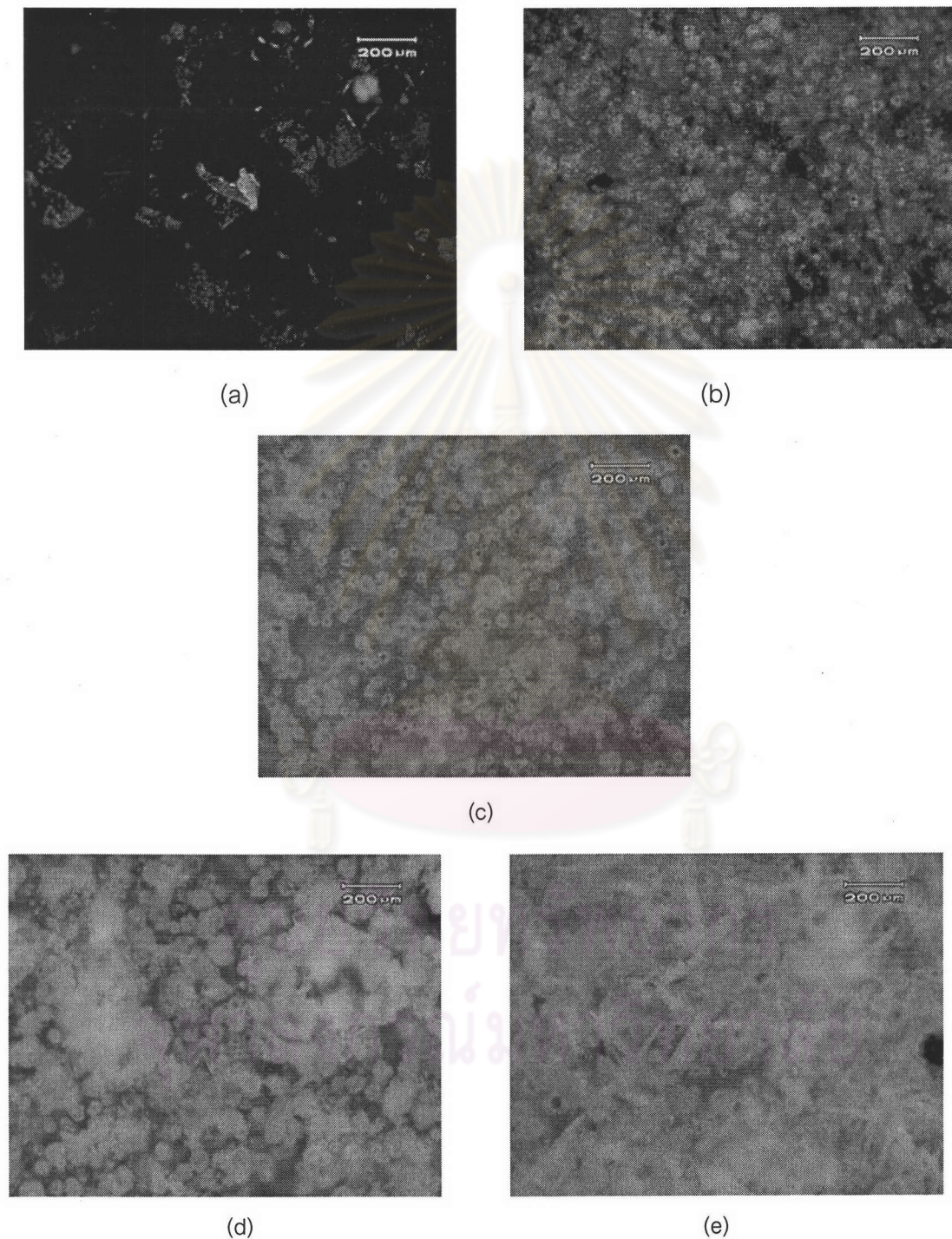


Figure 4.1 Optical micrographs of 50x magnified film surface

(a) -5 mA/cm^2 , (b) -7 mA/cm^2 , (c) -10 mA/cm^2 , (d) -15 mA/cm^2 , and (e) -20 mA/cm^2 for 3 minutes deposition time.

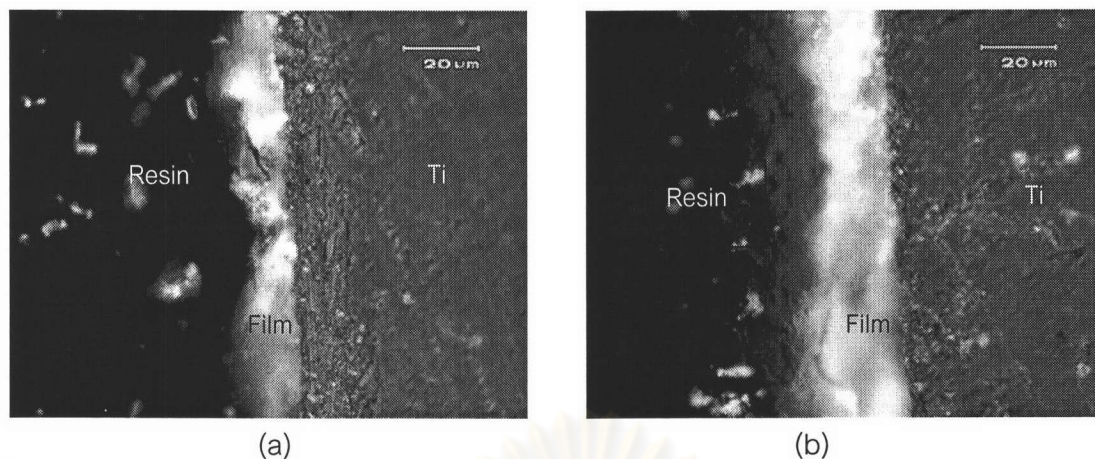


Figure 4.2 Optical micrograph of the thickness of as-deposited film at (a) 3 minutes and (b) 5 minutes.

From the above Figure, the thickness of the films from Figure 4.2(a) and (b) are $15\ \mu\text{m}$ and $20\ \mu\text{m}$, respectively. It is easily seen that their thickness are increased with increasing deposition time.

4.1.1.1 X-ray diffraction pattern

XRD pattern of calcium phosphates thin film from MCPM based aqueous electrolytes for 3 and 5 minutes deposition times are shown in Figure 4.3

From Figure 4.3, the obtained phases on these thin films were different depending on deposition times. The thin film specimens gained with 3 minutes deposition time showed only one existing phase of brushite on titanium substrate while the thin film specimens gained with 5 minutes deposition time showed two phases, brushite (major phase) co-existed with monetite (minor phase).

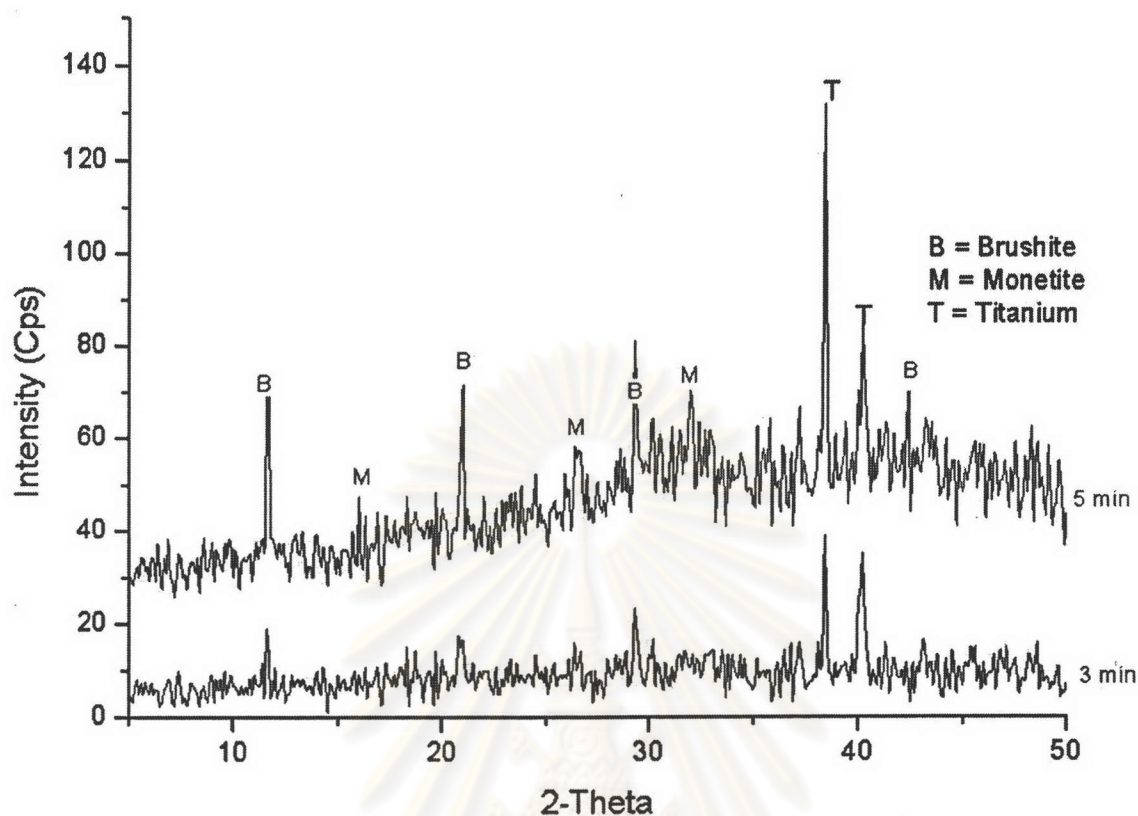
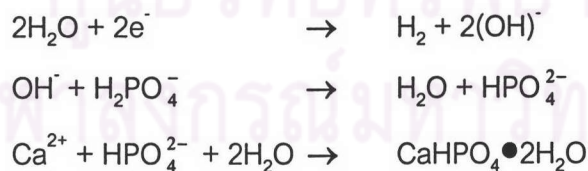


Figure 4.3 XRD pattern of calcium phosphates thin film gained from MCPM based aqueous electrolyte at -10 mA/cm^2 for 3 and 5 minutes.

The possible reactants of MCPM based aqueous solution should be H^+ , H_2O , O_2 , $\text{H}_2\text{PO}_4^{2-}$, and Ca^{2+} . Therefore, the related possible reactions of aqueous solutions might be:



AND



So, the deposition of brushite and/or monetite was mainly caused by migration. Although, monetite is not as stable as brushite in air but it is still existed when reaction occurred at the same current but longer time because as-deposited brushite might

pulled more water from MCPM based aqueous electrolyte into itself. Then, monetite still existed and also quite stable.

4.1.1.2 Scanning electron microscope

Scanning electron micrographs, Figure 4.4-4.5 show that the films were porous.



Figure 4.4 SEM micrographs calcium phosphates film gained from MCPM based aqueous electrolyte at -10 mA/cm^2 for 3 minutes at (a) 1,000x and (b) 7,500x respectively.

From Figure 4.4, and 4.5 the microstructure of films were a porous films with multi-crystals phases. Moreover, there were some voids, which were easily seen from SEM micrographs that might occurred during electrolytic deposition process. In addition, film at 5 minutes deposition time had less porosity than the 3 minutes one.

Anyway, brushite microstructure was plate-like shape, while monetite was rod shape (monoclinic). These calcium phosphates film might deposit along its reaction lines. That's why calcium phosphate thin film microstructures were combination of each single phases, which seem to be deposited in only one direction, into porous microstructure.

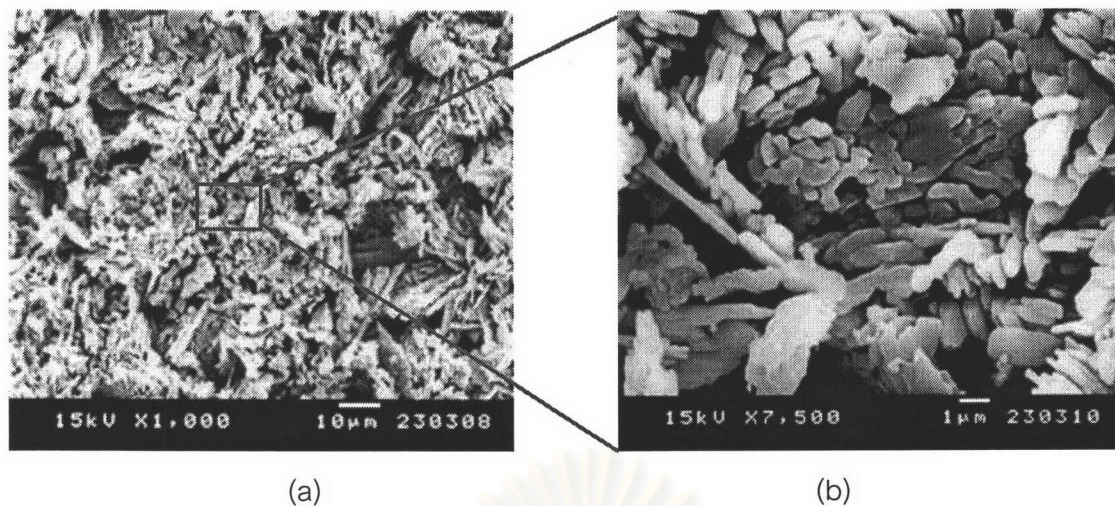


Figure 4.5 SEM micrographs calcium phosphates film gained from MCPM based aqueous electrolyte at -10 mA/cm^2 for 5 minutes at (a) 1,000x and (b) 7,500x respectively.

4.1.1.3 Scratch test for scraped adhesion

The specimens for scratch test selected from its thickness and surface appearance. Calcium phosphates films with 5 minutes deposition time showed better appearance than the films with 3 minutes deposition time. Moreover, film thickness also thicker than the latter. After testing under load applied, the film still remained on substrates up to 150g applied load (Figure 4.6). Its shear stress, which determined by the equation from section 3.4.5, was 8.83 MPa.

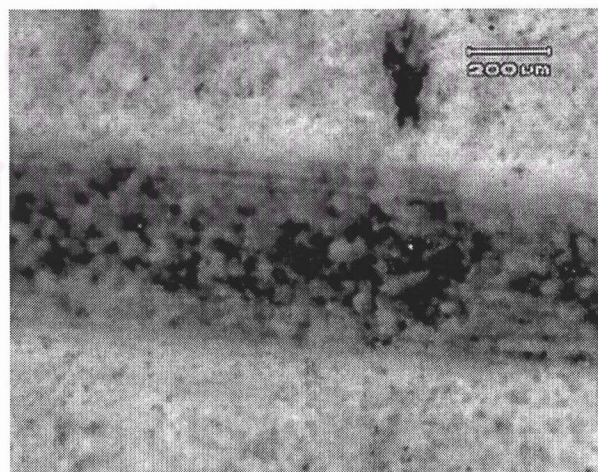


Figure 4.6 Scratch trace of as-deposited film that gained from MCPM based aqueous electrolyte at -10 mA/cm^2 , 5 minutes deposition time.

4.1.2 After interval times in R-SBF

The specimens, which were from those two picked up conditions (-10 mA/cm^2 at 3 and 5 minutes deposition time) were soaked in R-SBF for 2, 4, and 8 hours respectively. The films surface observed by OM are as shown in figure 4.7.

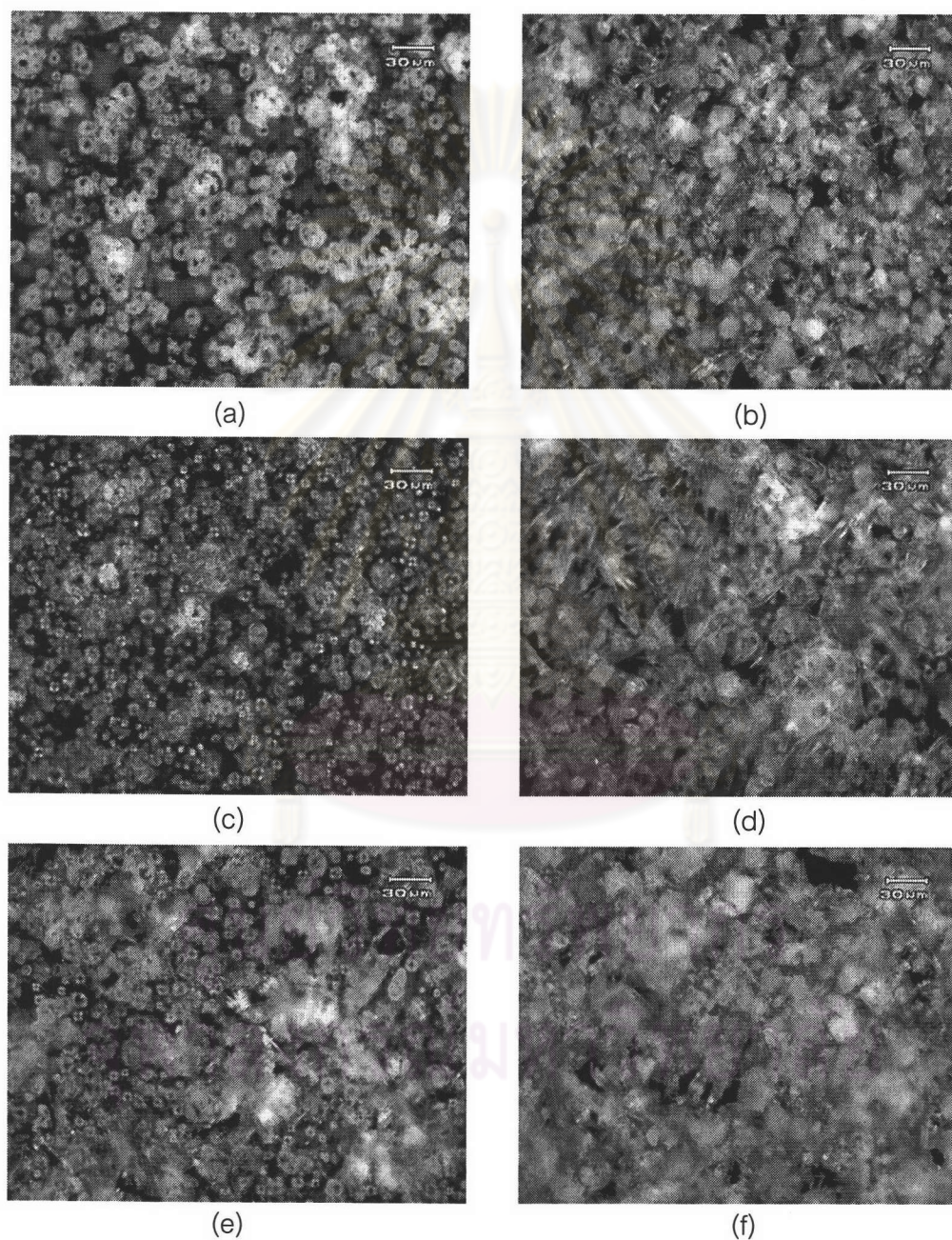


Figure 4.7 The films surface after soaking in R-SBF observed by OM at 200x. (a), (b), and (c) are 3 min. deposited time film surfaces for 2, 4, and 8 hours. (d), (e), and (f) are 5 min. deposited time film surfaces for 2, 4, and 8 hours.

4.1.2.1 X-ray diffraction pattern

To investigate films phases if it changed during R-SBF, XRD pattern also used in this investigation by comparison its as-deposited film to R-SBF films XRD pattern as shown in figure 4.8 and 4.9.

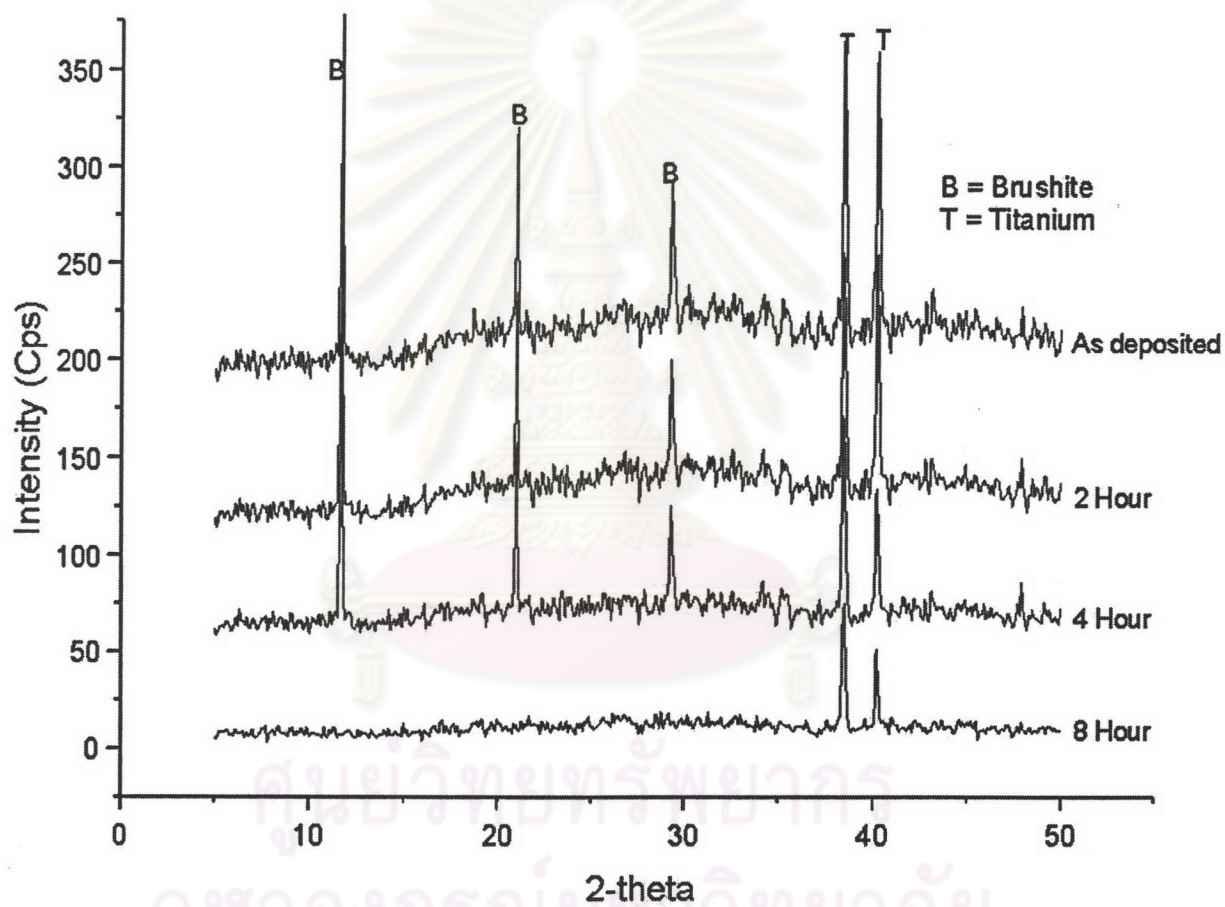


Figure 4.8 XRD pattern of the 3-min as-deposited film after soaking in R-SBF for 2, 4 and 8 hours.

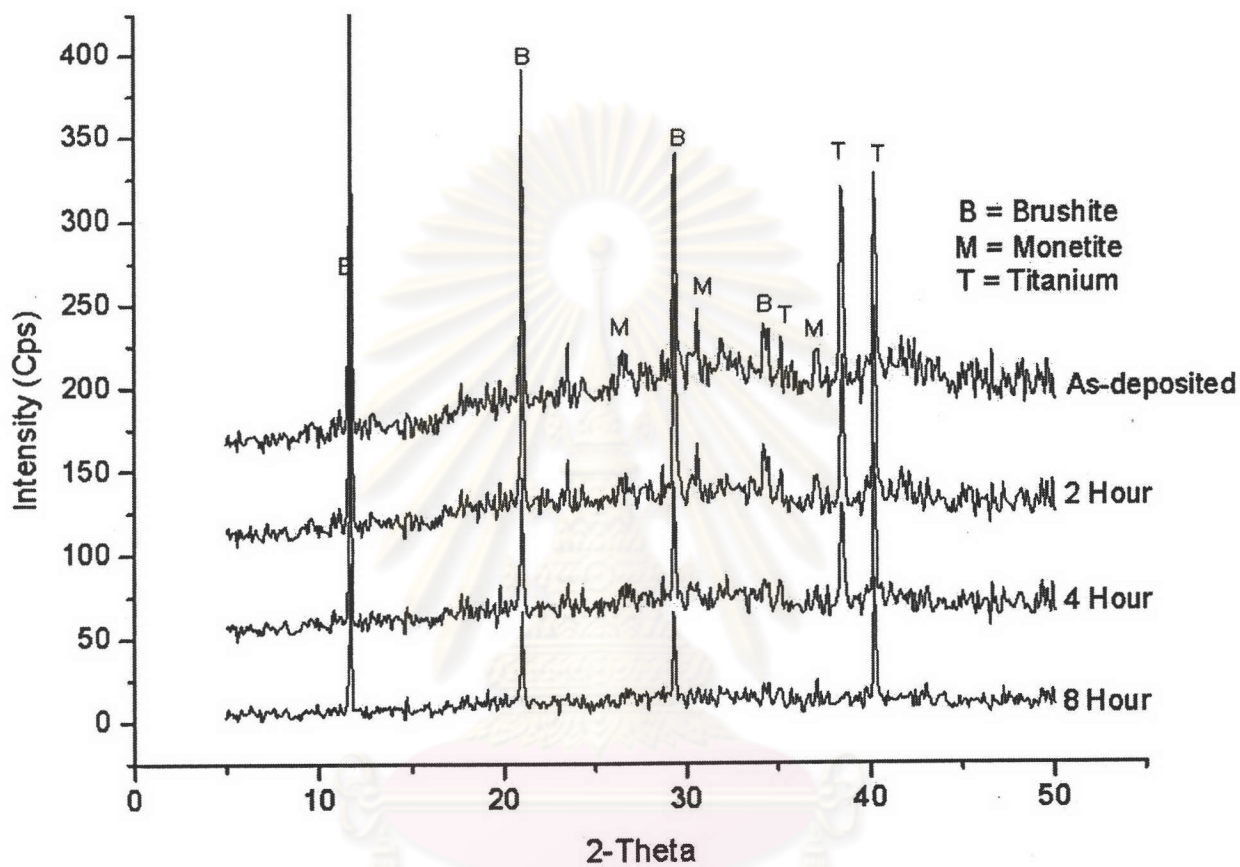


Figure 4.9 XRD pattern of the 5-min as-deposited film after soaking in R-SBF for 2, 4 and 8 hours.

4.1.2.2 Scanning electron microscope

From its XRD pattern results, films surface might be slightly changed according to peak intensity, which was decreasing. Then, SEM photograph of film surface after R-SBF are shown in following Figures:

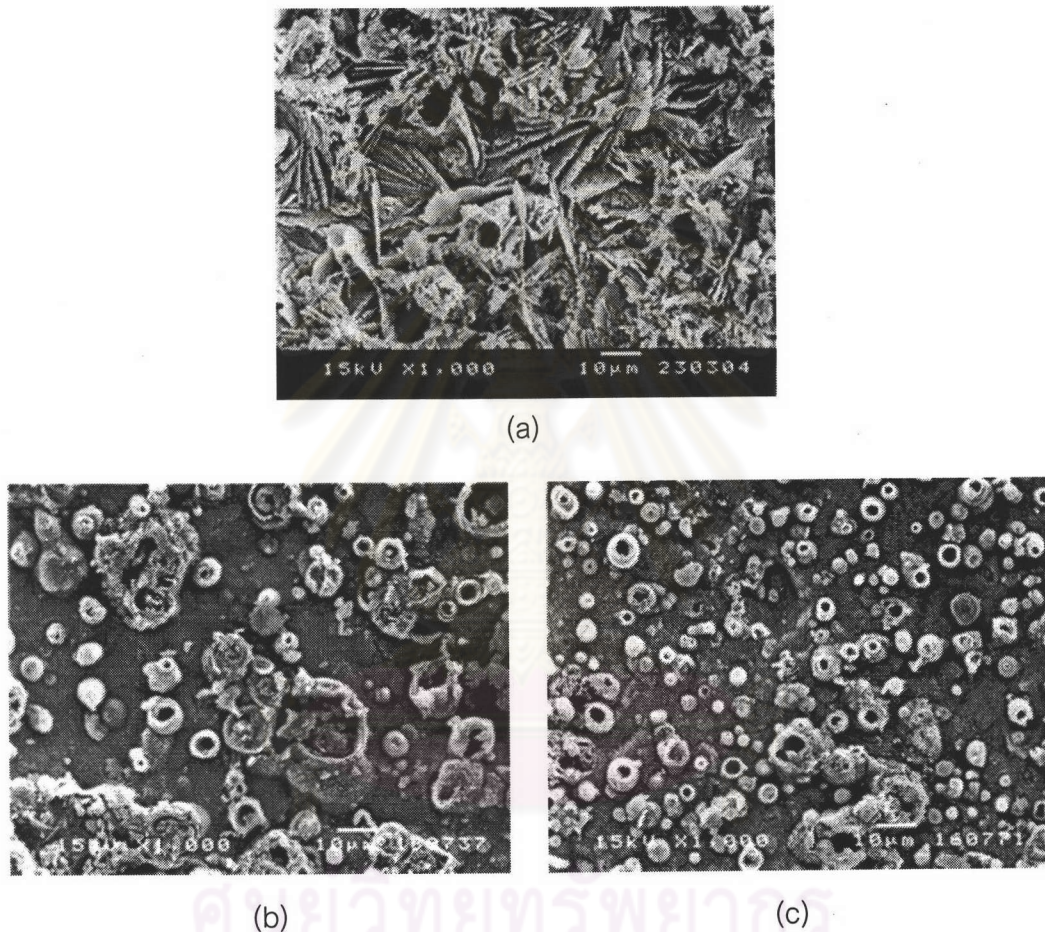


Figure 4.10 SEM micrographs of (a) the 3-min as-deposited film before soaking in R-SBF compared to after soaking in R-SBF for (b) 2 hrs, and (c) 8 hrs.

It could be seen that crystal morphology of the 3-min as-deposited film was changed to needle-like shape. However, brushite phase (plate-like crystal structure) still remained in the films after soaking in R-SBF for 2 hours that was in agreement to its XRD pattern (Figure 4.8). Brushite phase was not appeared in both SEM micrographs and its XRD pattern after soaking in R-SBF for 8 hours. It might be that all brushite phase was

completely converted to bone-like apatite* which are a very fine primary crystal completely covered the former phase surfaces.

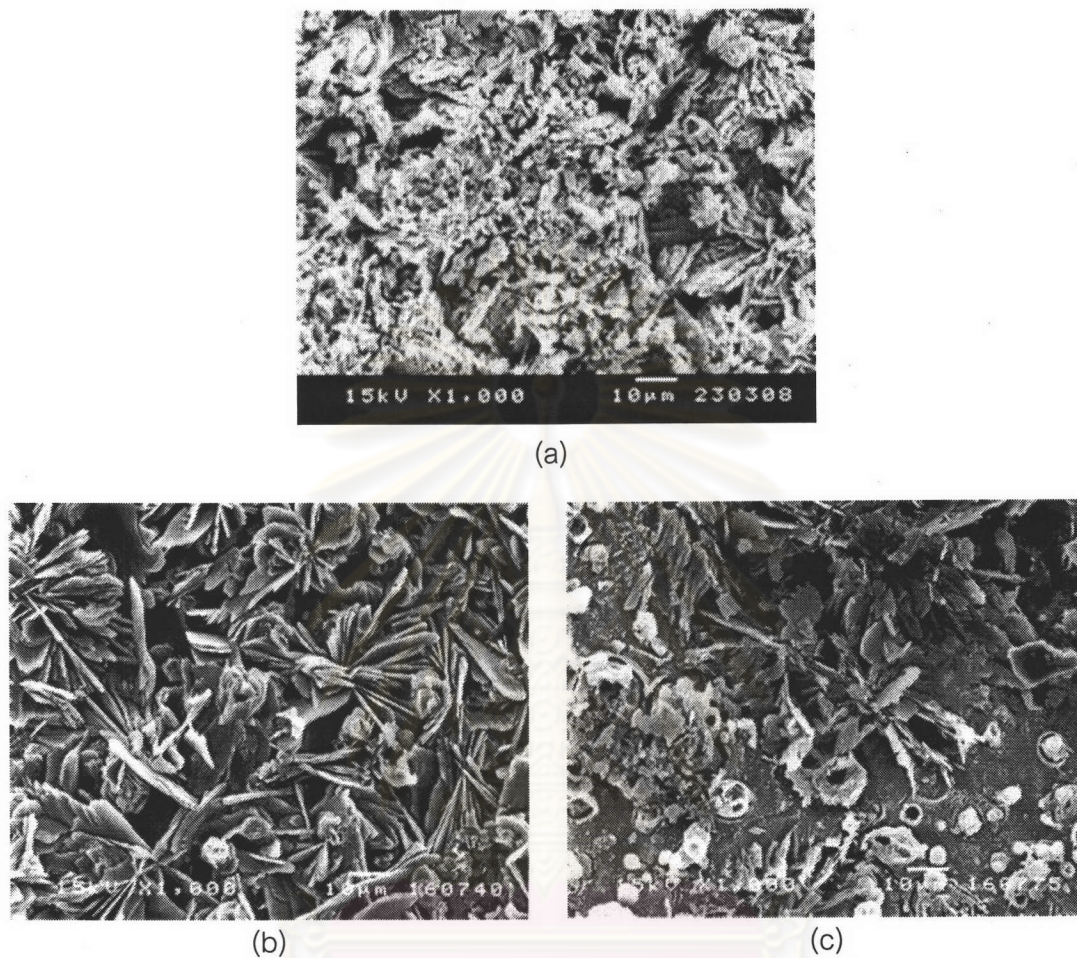


Figure 4.11 SEM micrographs of (a) the 5-min as-deposited film before soaking in R-SBF compared to after soaking in R-SBF for (b) 2 hrs, and (c) 8 hrs.

For 5-min deposition time, all specimens, which were soaked in R-SBF, still showed brushite phase but the quantity was decreased with increasing the soaking time. Bone-like apatite also appeared in needle-like shape** that was in agreement to its XRD pattern from Figure 4.9.

* See Appendix D for more details.

** See Appendix E for more details.

For 8 hours soaking time in R-SBF, brushite film was not completely converted to bon-like apatite comparable to the 3-min as-deposited film at the same soaking time because the 5-min film was thicker than the 3-min film. So, it might took longer time to convert all brushite into bone-like apatite.



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4.2 MCPM electrolyte based aqueous solution with ions addition

4.2.1 As-deposited films

In this condition, the electrolytes were divided into three sub-groups as already described in section 3.1.1. The first one was MCPM electrolyte based aqueous solution with 0.15 g NaF and 21g NaNO₃ addition (formula I). The current density that the film could formed on titanium substrates was -20 mA/cm^2 for 3 and 5 minutes of deposition time. Their film surfaces observed by OM were shown in figure 4.12.

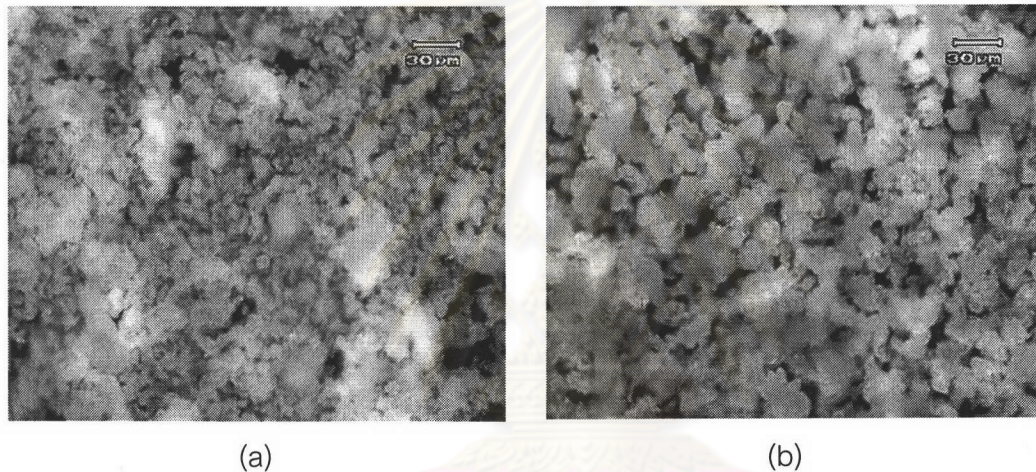


Figure 4.12 Films surface gained from MCPM electrolyte based aqueous solution with ions addition (formula I) at -20 mA/cm^2 for (a) 3 mins and (b) 5 minutes.

The second formula was MCPM electrolyte based aqueous solution with 0.10 g NaF and 14 g NaNO₃ additives. The current density that the film could formed on titanium substrates was -15 mA/cm^2 for 3 and 5 minutes deposition time. Their film surfaces observed by OM were shown in figure 4.13.

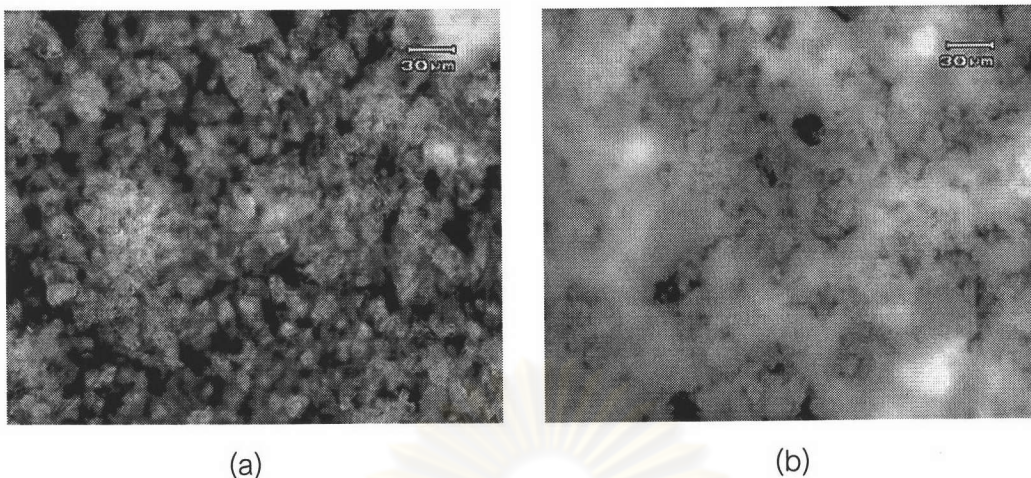


Figure 4.13 Films surface gained from MCPM electrolyte based aqueous solution with ions addition (formula II) at -15 mA/cm^2 for (a) 3 mins and (b) 5 minutes.

The third formula was MCPM electrolyte based aqueous solution with 0.05 g NaF and 7g NaNO_3 addition. The current density that the film could form on titanium substrates was -10 mA/cm^2 for 3 and 5 minutes of deposition time. Their film surfaces observed by OM were shown in figure 4.14.

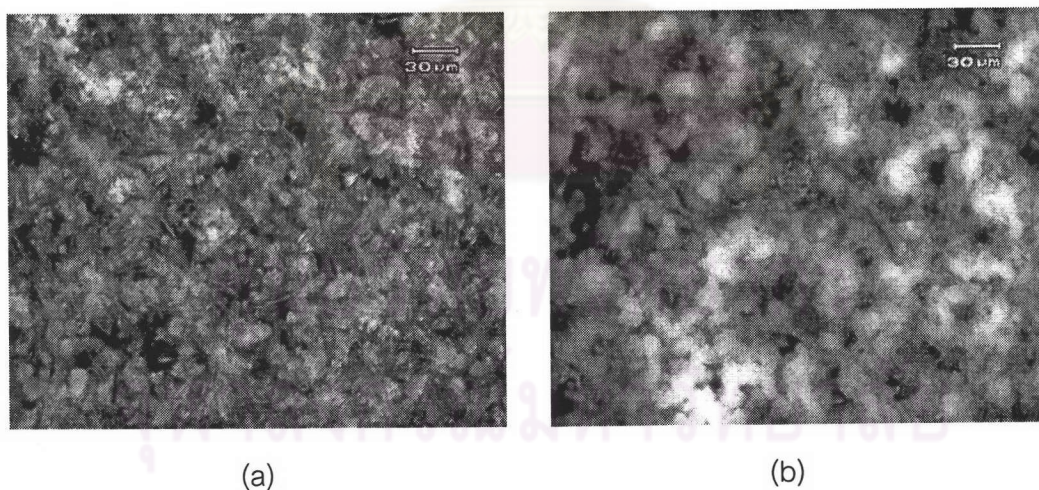
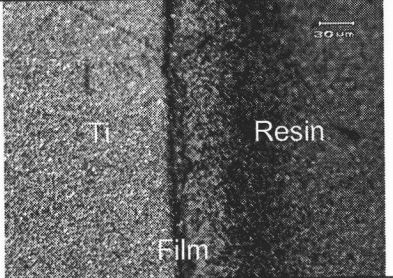
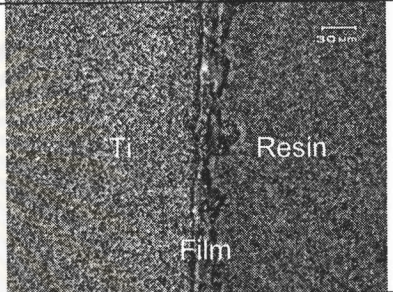
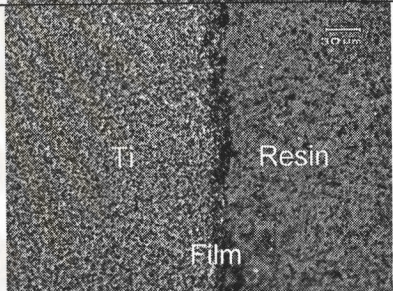
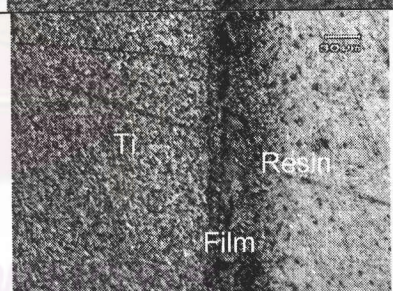
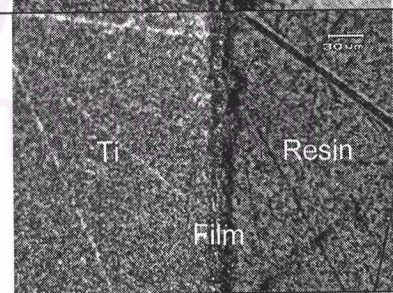
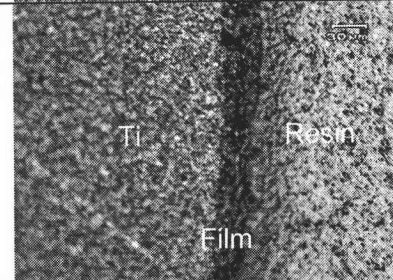


Figure 4.14 Films surface gained from MCPM electrolyte based aqueous solution with ions addition (formula III) at -10 mA/cm^2 for (a) 3 mins and (b) 5 minutes.

Table 4.1 Films thickness obtained from each formula of ions adding.

Conditions		Thickness	Photograph (200X)
Formula I	3 min	10 μ m	
	5 min	25 μ m	
Formula II	3 min	13 μ m	
	5 min	25 μ m	
Formula III	3 min	15 μ m	
	5 min	27 μ m	

From that all the above micrographs by OM, there was no significant difference in film appearances among each formula. Three conditions produced porous films as same as the films gained from section 4.1.1. Then, their XRD pattern and SEM results would be used to make the decision to select the specimens for the further experiments.

4.2.1.1 X-ray diffraction pattern

XRD patterns of all above electrolytes are shown in the following figure 4.15.

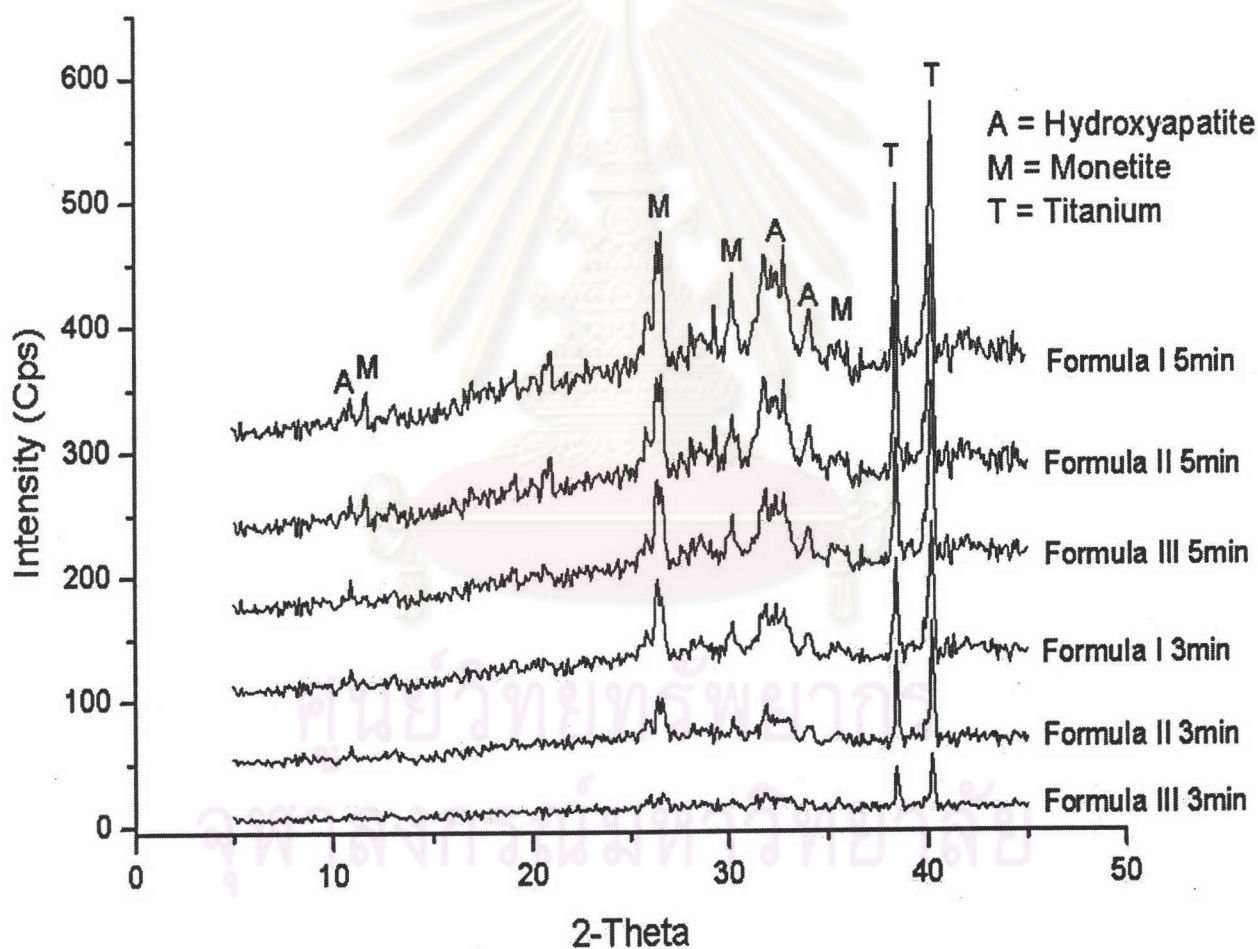


Figure 4.15 XRD pattern showed phases contained in thin films from different ions addition formula produced by MCPM electrolyte based aqueous solution at the deposition time for 3 and 5 minutes.

XRD patterns showed that the amount of additive ions was affected to hydroxyapatite formation. At higher amount of ions adding, the rate of hydroxyapatite formation increased. Moreover, for longer deposition time, more crystallization occurred. The highest intensity peaks of hydroxyapatite appeared in a formula I at 5-minutes of deposition time. This is the criterion that this specimen implied the higher amount of hydroxyapatite was formed in this specimen.

The specimens, which gained from MCPM electrolyte based aqueous solution with ions addition, showed two phases – monetite co-existed with hydroxyapatite. The related possible reactions of hydroxyapatite might occur as follows:



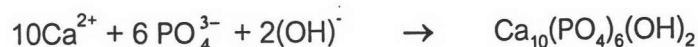
The local concentration of acid phosphate HPO_4^{2-} should be effected by the following equilibrium:



or



When extra OH^- was afforded, including NaNO_3 and NaF were effective for the formation of HAp and remarkably enlarged the formation region, HAp could be deposited on the substrates by the following reaction:



4.2.1.2 Scanning electron microscope

Scanning electron microscope, which was used to investigate films microstructure have been found that the films, were existed in porous film. SEM micrographs of the specimen formed by formula I at both deposition times of 3 and 5 minutes were shown in figure 4.16.

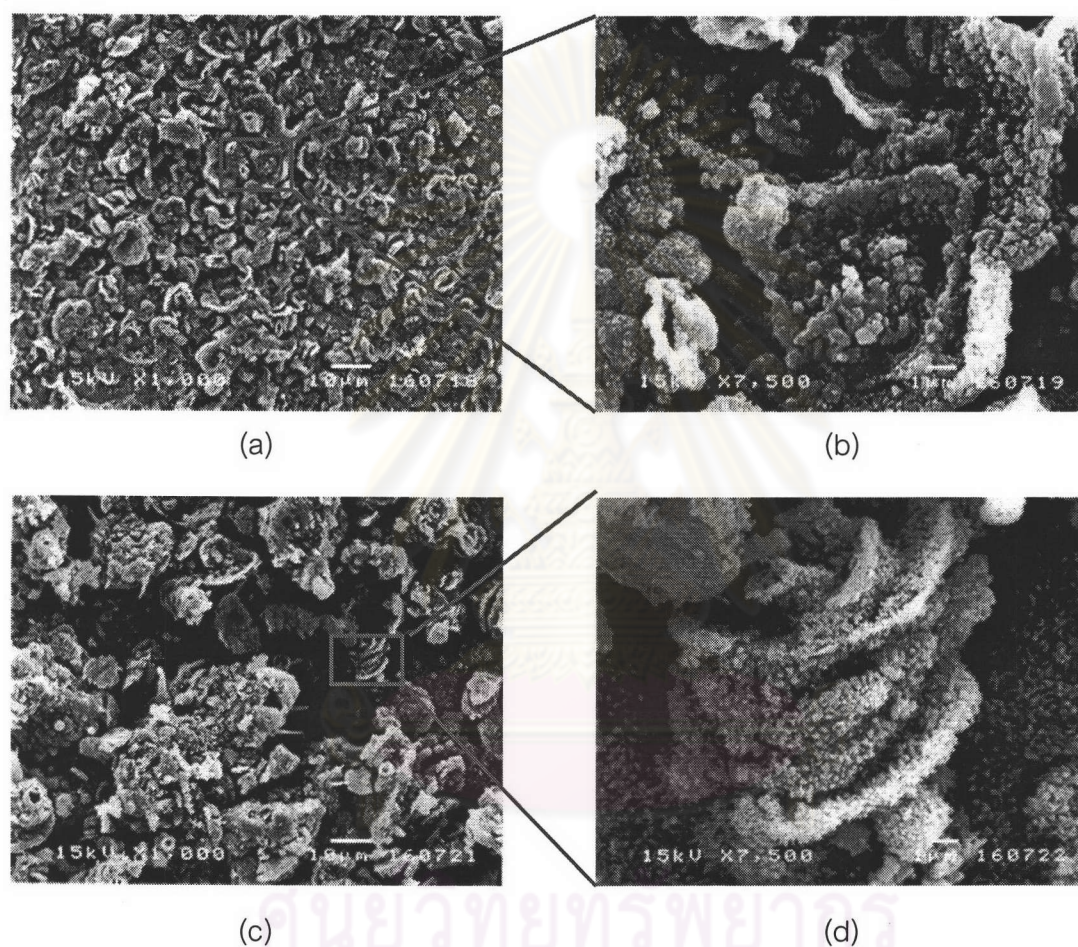


Figure 4.16 SEM micrographs of the film surfaces obtained from MCPM electrolyte based aqueous solution with ions adding (formula I) at -20 mA/cm^2 for 3 mins at (a) 1,000x (b) 7,500x, and 5 mins at (c) 1,000x (d) 7,500x .

From figure 4.16, it could be seen that a very fine crystal of HAp was completely covered the substrate. HAp*, however, might cover only on the specimens surfaces because their XRD results still showed monetite phase remained even in the shortest

* See Appendix F for more details.

deposition time. That means the amount of monetite was increased with increasing deposition time. The amount of hydroxyapatite also increased with increasing deposition time.

4.2.1.3 Scratch test for scraped adhesion

The specimens in formula I with 5 minutes of deposition time were selected for scratch test because its XRD pattern show the highest HAp content. After testing under load applied, the film still attached on substrates up to 100g applied load (Figure 4.17). Its shear stress, which determined by the equation from section 3.4.5, was 5.89 MPa.

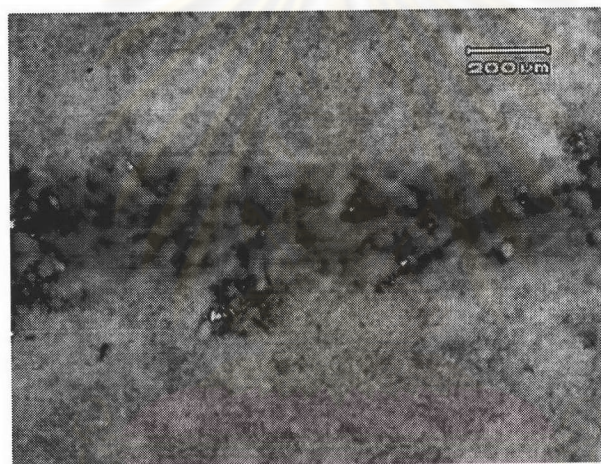


Figure 4.17 Optical micrograph of scratch trace of as deposited film that obtained from MCPM electrolyte based aqueous solution with additive ions (formula I) at -20 mA/cm^2 , 5 min deposition time.

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4.2.2 After interval times in R-SBF

All specimen from formula I were soaked in R-SBF for 2, 4, and 8 Hour respectively. The films surface were observed by OM are as shown in figure 4.18.

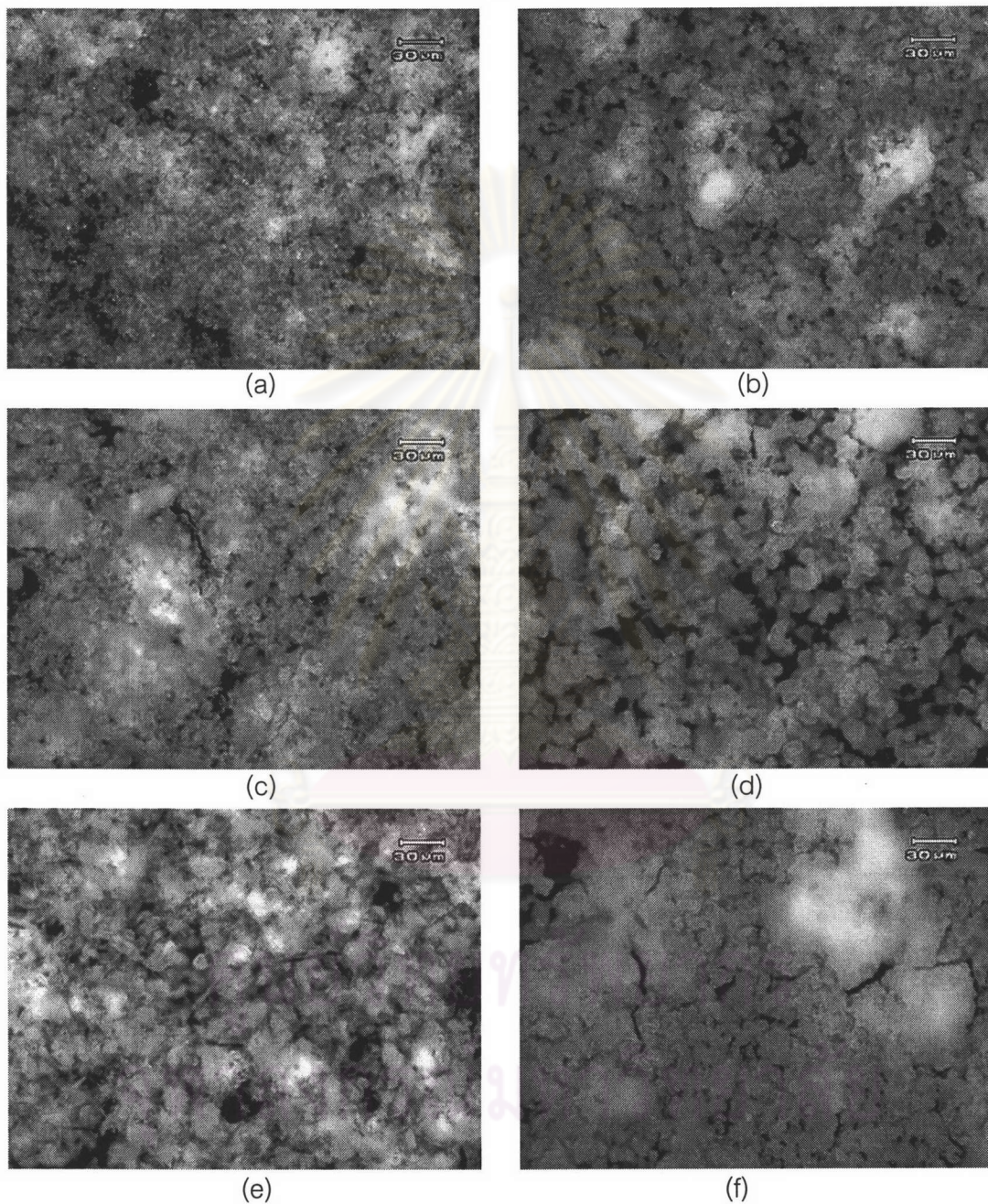


Figure 4.18 Optical micrographs of the films surface after soaking in R-SBF magnified at 200x, (a), (b), and (c) were the film surfaces at the deposition time for 3 mins subjected to R-SBF for 2, 4, and 8 hrs, respectively, (d), (e), and (f) were the film surfaces at the deposition time for 5 mins subjected to R-SBF for 2, 4, and 8 hrs, respectively.

4.2.2.1 X-ray diffraction pattern

From OM micrographs, it could be seen that the film surface had changed. Then, XRD was used to investigate their morphology changes in those specimens.

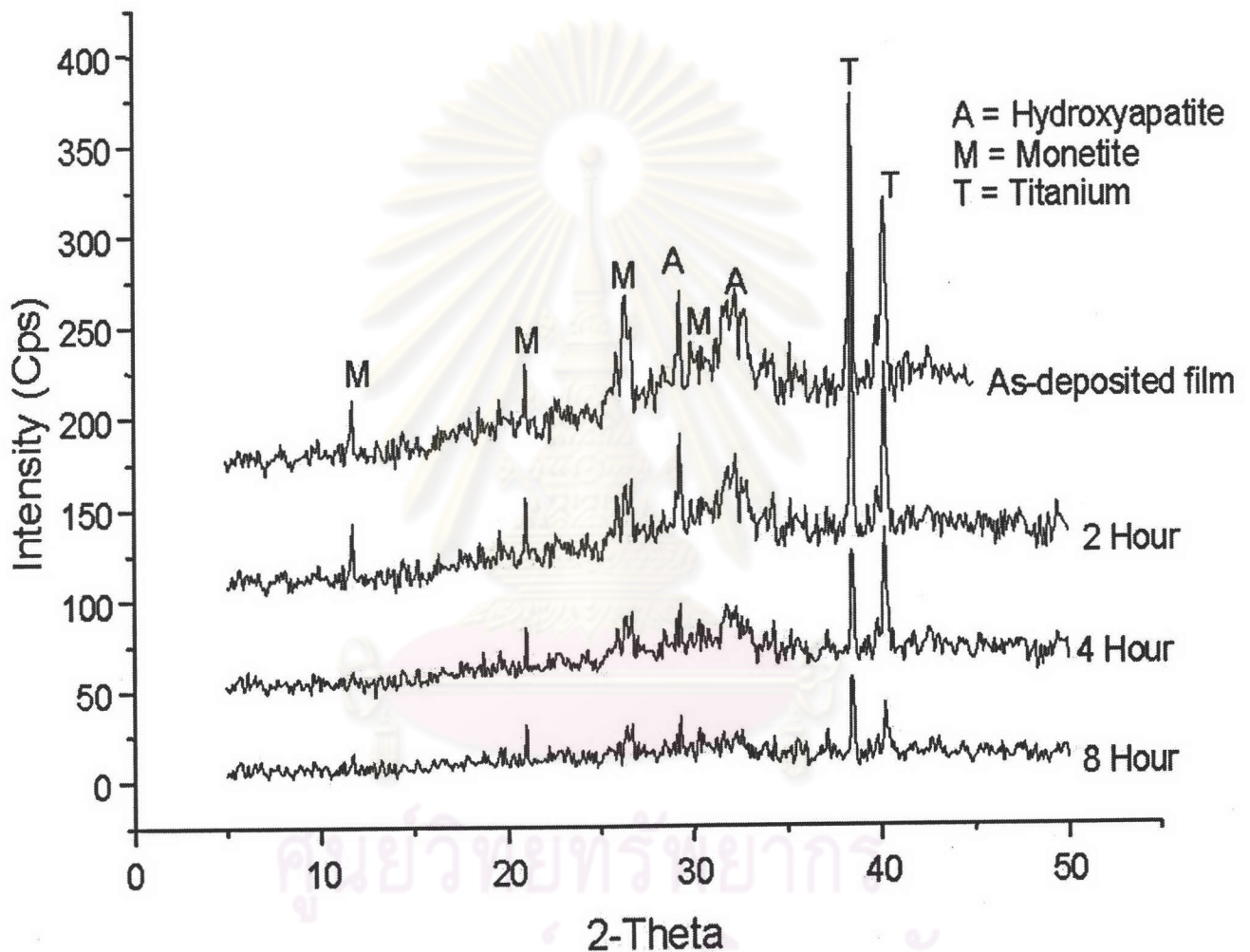


Figure 4.19 XRD patterns of the 3-mins as-deposited film from MCPM electrolyte based aqueous solution with ions addition after soaking in R-SBF for 2, 4 and 8 hours.

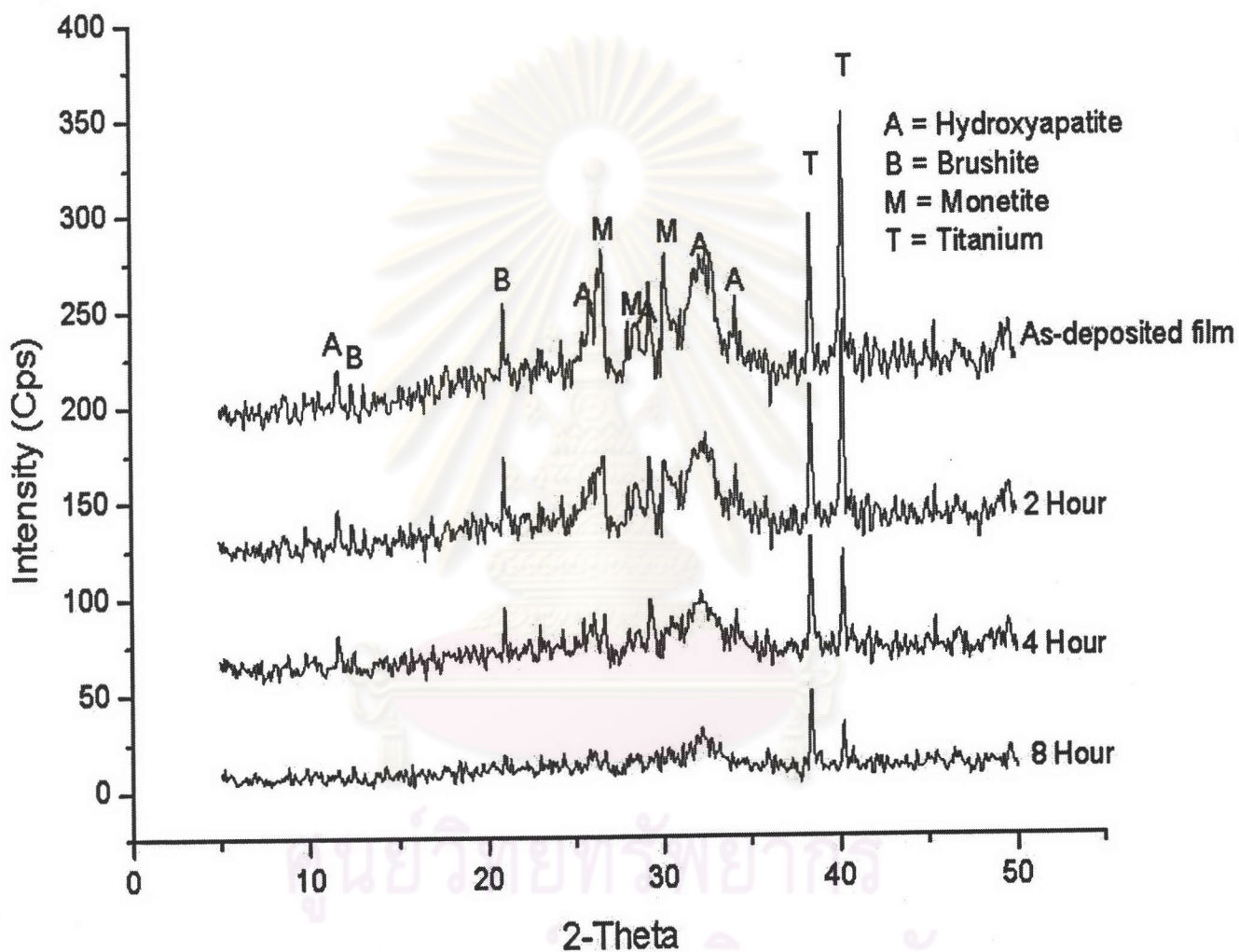


Figure 4.20 XRD patterns of the 5-mins as-deposited film from MCPM electrolyte based aqueous solution with ions addition after soaking in R-SBF for 2, 4 and 8 hours.

4.2.2.2 Scanning electron microscope

From their XRD results, films surface might be changed according to the decreasing of peak intensity with longer soaking time. Then, SEM micrographs of film surface after soaking in R-SBF shown in following figures in comparison with its as deposited film surfaces:

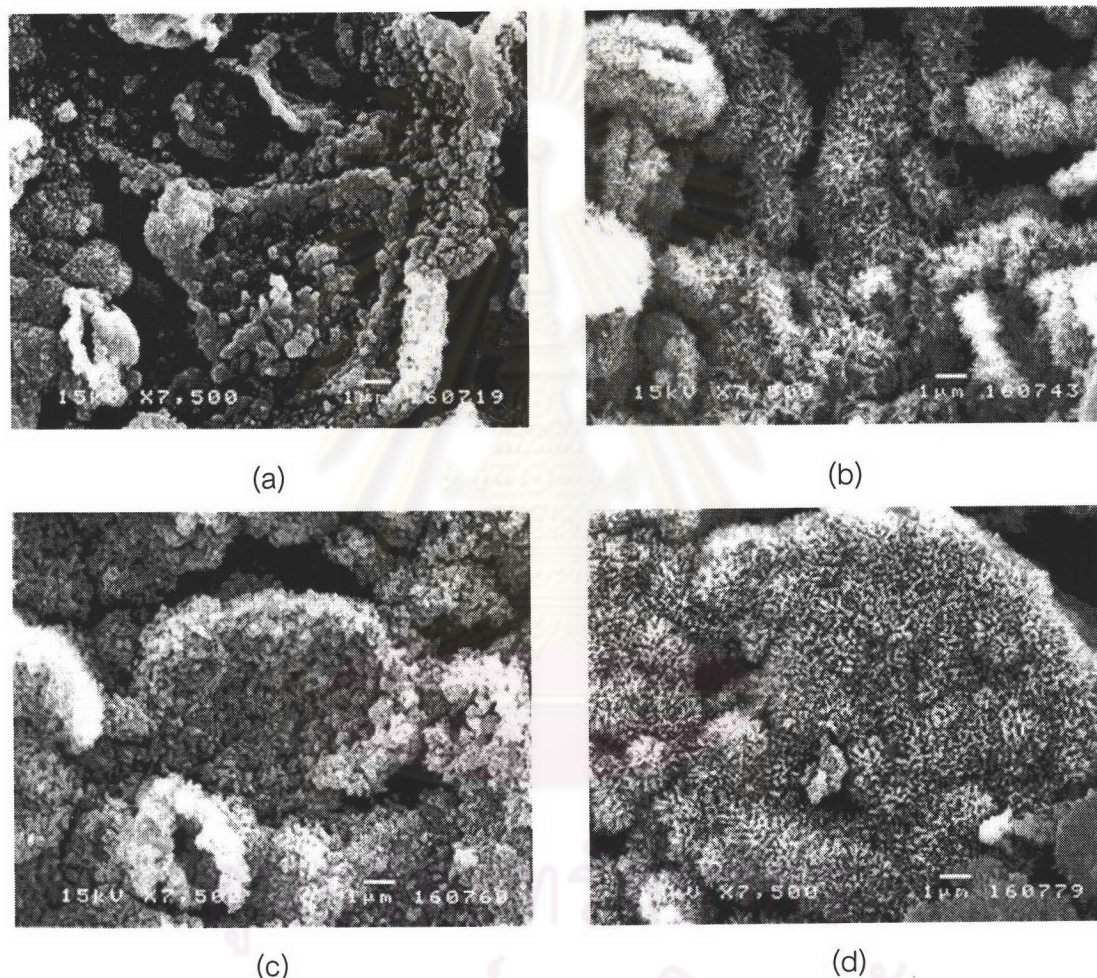


Figure 4.21 SEM micrographs of (a) The 3-mins as deposited film from MCPM electrolyte based aqueous solution with ions addition before soaking in R-SBF compared to the film after soaking in R-SBF for (b) 2 hrs, (c) 4 hrs, and (d) 8 hrs.

It could be seen from both XRD patterns and SEM micrographs that film surfaces had covered with a lot of needle-like fine crystal structure which might be HAP according to its XRD pattern (Figure 4.19). Moreover, its XRD peak intensity tended to decrease with increasing soaking time in R-SBF. It might occur from some of monetite

phase, which was dissolved into SBF and precipitated back to formed very fine primary crystal of HAp^{*}, was not completely converted itself to HAp and still remained in the films.

SEM micrographs of the 5-mins as-deposited film of MCPM electrolyte based aqueous solution with ions addition before soaking in R-SBF compared to the 5-mins film after soaking in R-SBF at three different interval times are shown in figure 4.22.

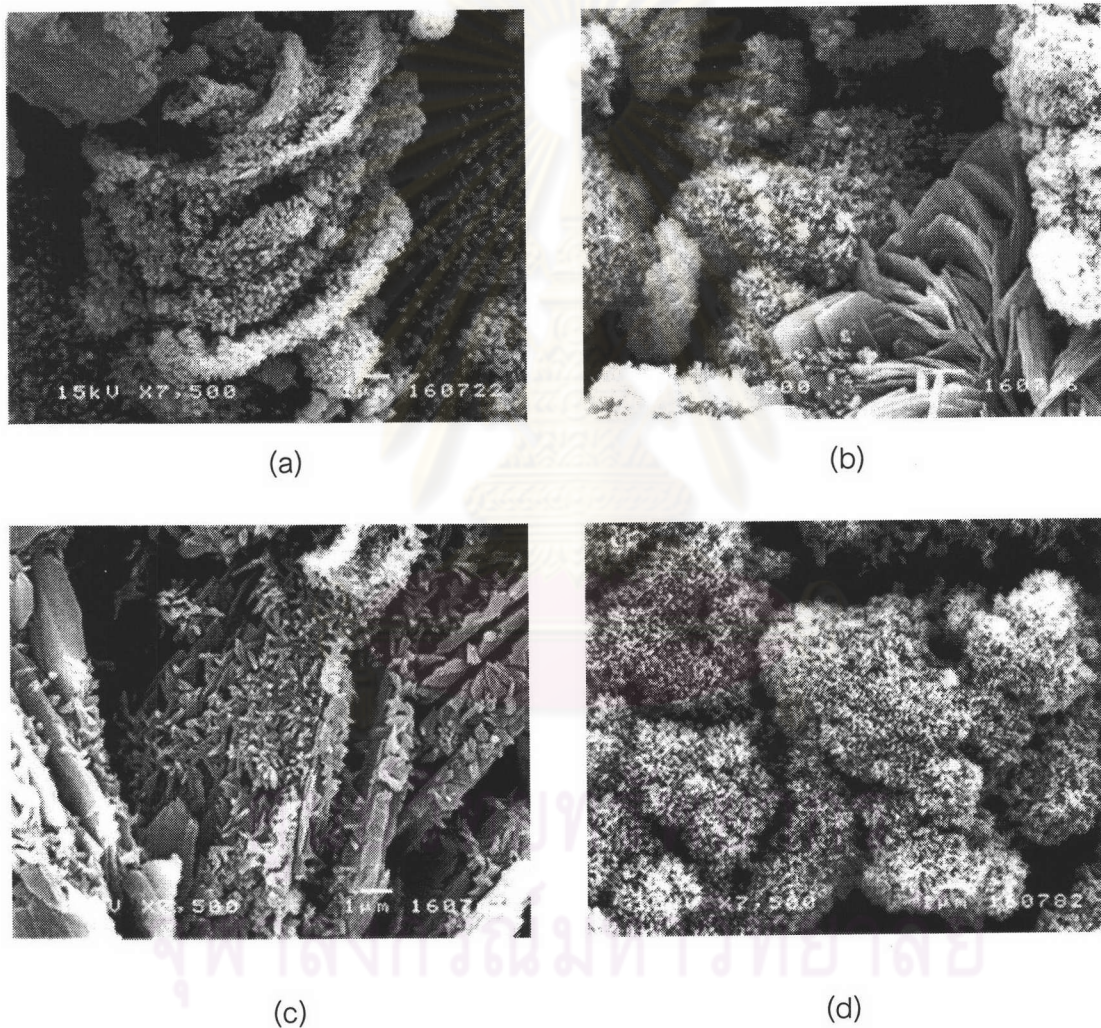


Figure 4.22 SEM micrographs of (a) The 5-min as deposited film from MCPM electrolyte based aqueous solution with ions addition before soaking in R-SBF compared to the film after soaking in R-SBF at (b) 2 hrs,(c) 4 hrs, and (d) 8 hrs.

* See Appendix F for more detail.

From figure 4.22 and its XRD pattern (figure 4.20) showed that the specimen with soaking time in SBF less than 4 hours would be mixed phases^{*}. According to XRD results, at 2 and 4 hours, the existing phases of film were HAp mixed with monetite and a little amount of brushite. In this case, brushite might be occurred during electrolytic deposition processes depending on the longer time of deposition. It has been known previously that brushite is more stable than monetite (from Ref. 37), so it is possible that brushite would exist in these films. The HAp, however, existed in very fine primary crystals affected to its XRD pattern at soaking time in R-SBF longer than 4 hours in which appeared as broadening peaks with lower intensity for other phases such monetite.



^{*}See Appendix G for more details.

4.3 MCPM electrolyte based 20% V/V and 50% V/V ethanol.

4.3.1 As-deposited films

In this study, 20% V/V and 50% V/V ethanol solutions were used as solvent for MCPM. The films obtained from these electrolytes observed by naked eyes were smoother than the others. The current density, which the films were formed, was -10 mA/cm^2 for 20% V/V and -20 mA/cm^2 for 50% V/V ethanol with the same deposition times as the former electrolytic deposition conditions. The film surfaces when observed by OM are shown in figure 4.23.

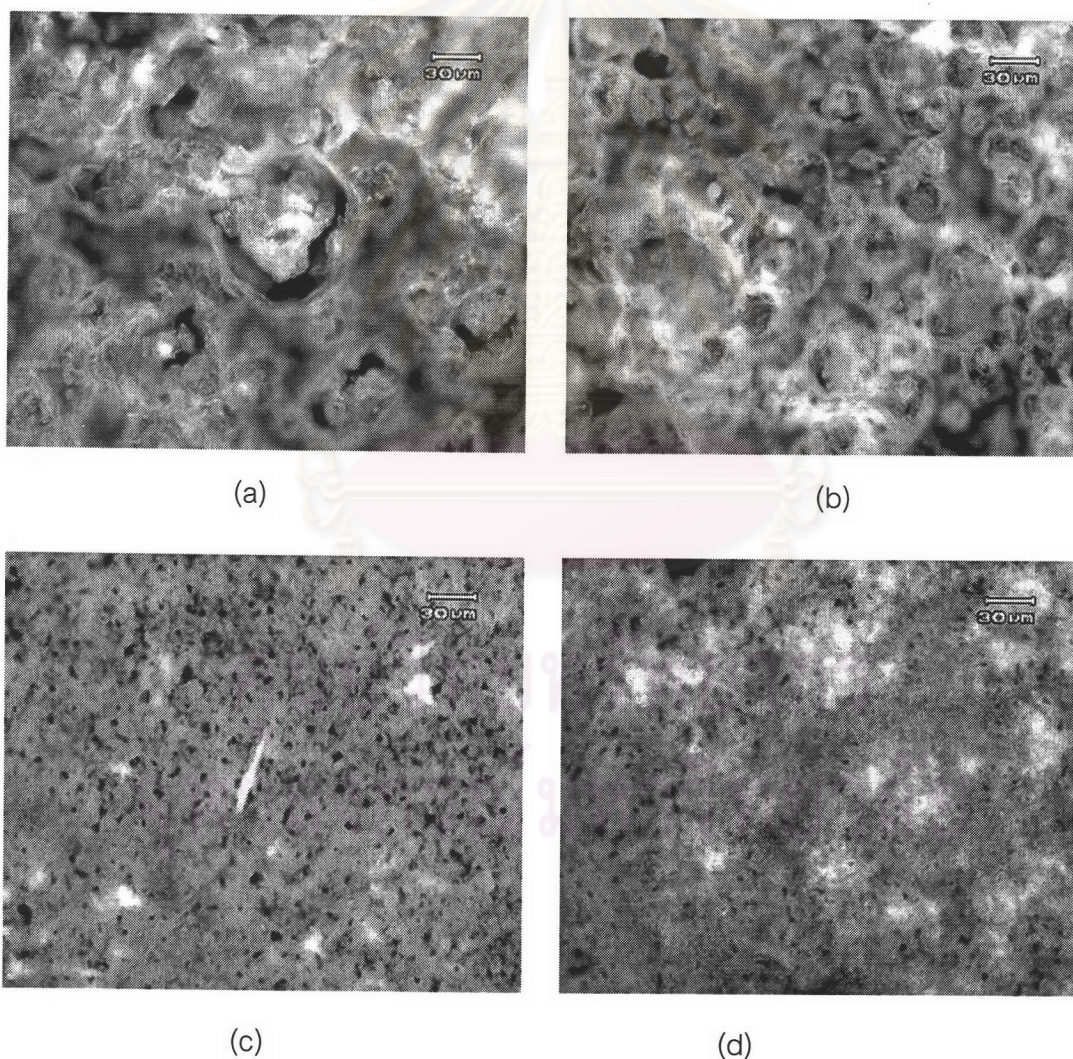


Figure 4.23 As-deposited film surface gained from MCPM electrolyte based 20% V/V ethanol solution at the deposition time for (a) 3 mins (b) 5 mins and 50% V/V ethanol solution at the deposition time for (c) 3 mins (d) 5 mins.

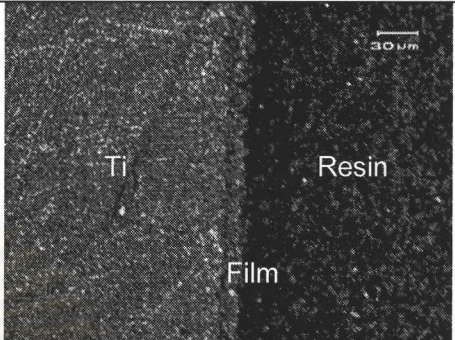
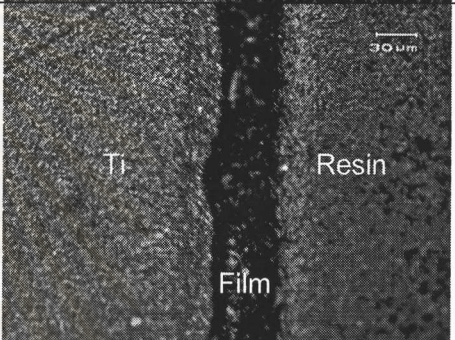
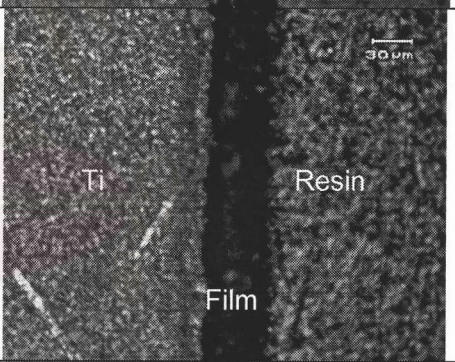
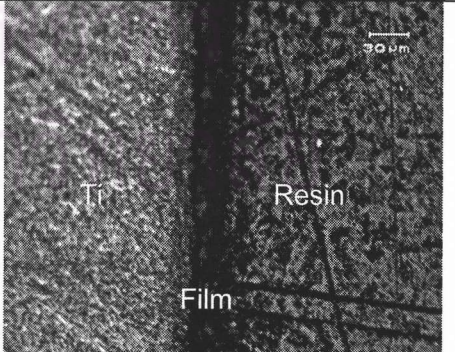
From all above figures, it was easily see that the films are really porous which formed as network structure and not strongly bonding with the substrates. Film thickness of these conditions also investigated by OM as shown in table 4.2

From all the following data, the deposition time was not affected much to film thickness because its deposition rate might be a little bit slow when compared to the other kind of electrolytes. Moreover, its crystal sizes were quite different. From figure 4.23, it could be seen that at MCPM electrolyte in 20% V/V ethanol, the crystal size was bigger than the one from 50% V/V ethanol.



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Table 4.2 Films thickness obtained from 20% V/V and 50% V/V ethanol based electrolytes.

Conditions		Thickness	Photographs (200x)
20% V/V ethanol	3 min	35 μ m	
	5 min	40 μ m	
50% V/V ethanol	3min	40 μ m	
	5min	40 μ m	

4.3.1.1 X-ray diffraction pattern

Phases existed in the films from above electrolytes were investigated from their XRD pattern as shown in figure 4.24.

From the XRD pattern, it could be seen that at 20% V/V ethanol, the film phases were existed in two phases, brushite co-existed with monetite. At the deposition longer time of 5 mins, monetite was a major phase while at the shorter time of 3 mins, brushite was a major phase. At 50% V/V ethanol, only monetite was existed.

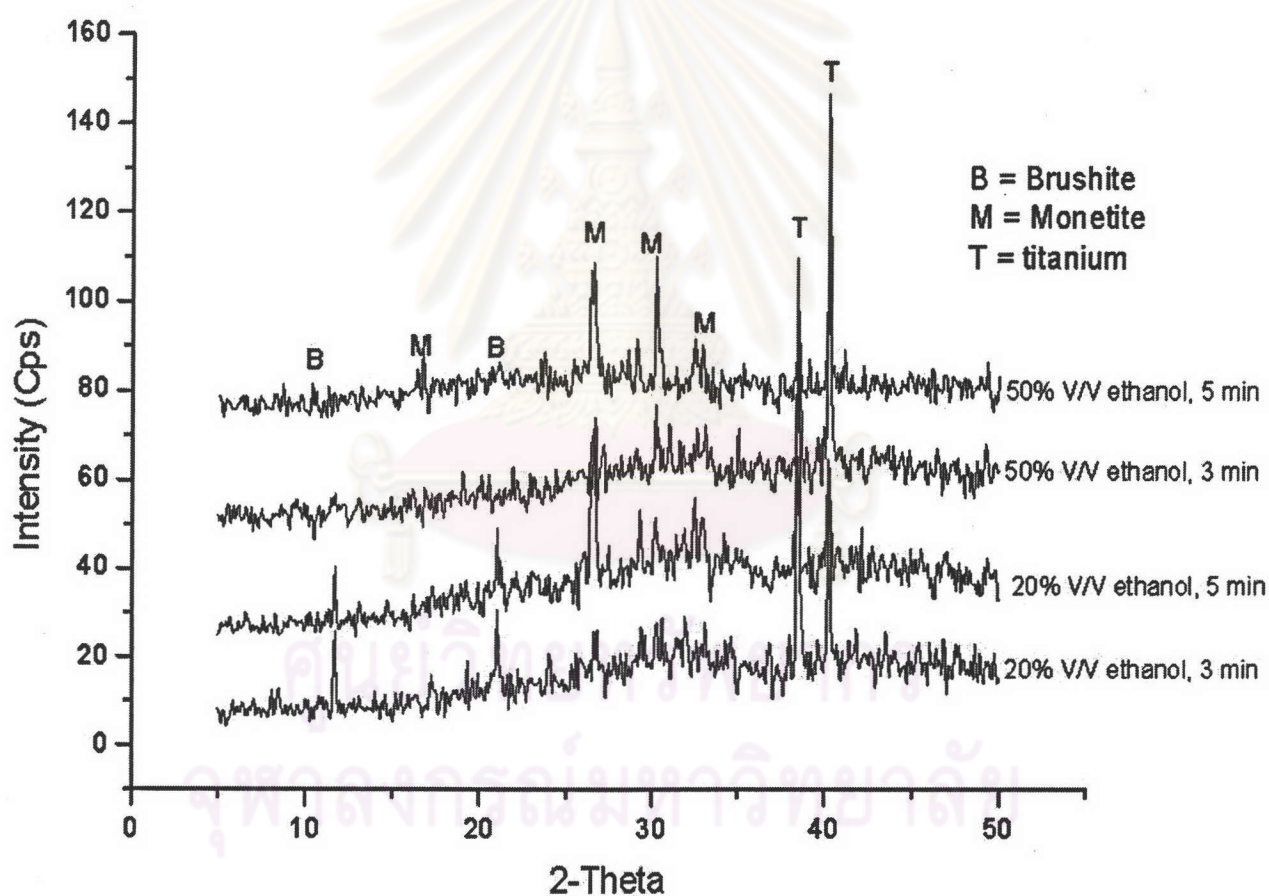
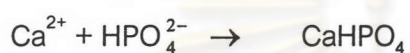
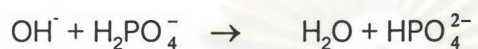


Figure 4.24 XRD patterns showed co-existed phases contained in thin films gained from MCPM electrolyte based 20% V/V and 50% V/V ethanol solutions at the different interval times.

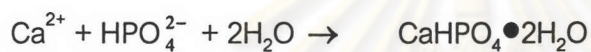
By the way, the possible reactions that might occur were:



When a large amount of OH^- is afforded, monetite could be deposited as a major phase, co-existed with a minor phase of brushite:



And




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4.3.1.2 Scanning electron microscope

The film microstructures were investigated by SEM in order to select the best condition for further study in R-SBF. Figure 4.25 showed the film microstructure which gained from 20% V/V and 50% V/V ethanol electrolytes.

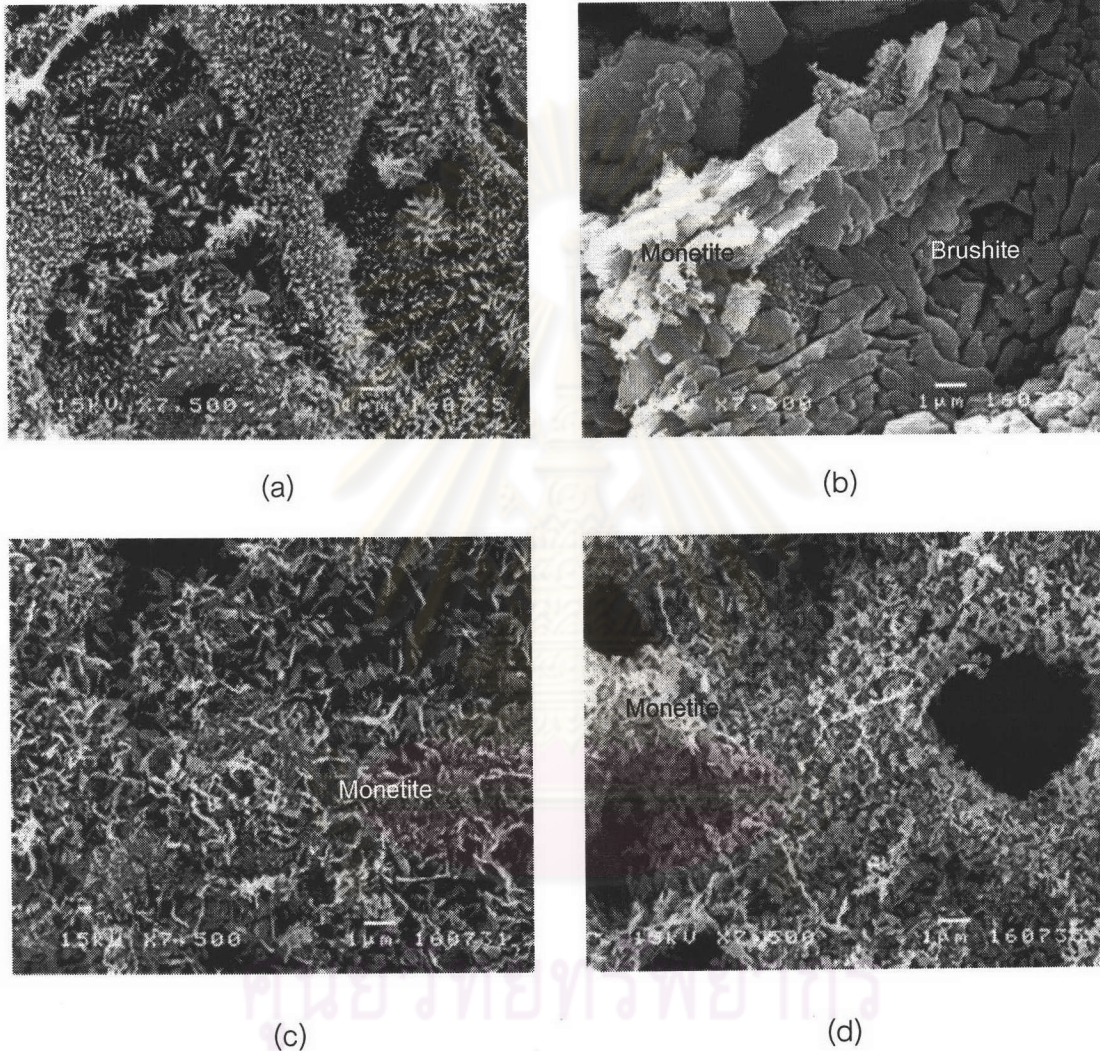


Figure 4.25 SEM micrographs of the film microstructures gained from MCPM based electrolyte based 20% V/V ethanol at (a) 3 mins, (b) 5 mins and 50% V/V ethanol at (c) 3 mins, (d) 5 mins.

From figure 4.25, it could be seen that two phases existed in 20% V/V ethanol, which was in agreement to its XRD results. On the other hand, 50% V/V ethanol showed only one phase existed of monetite with net work structure and not strongly bonded to its substrate. In figure 4.25(d) showed monetite network structure deposited on titanium

substrate by frictional force only. Moreover, there were many large pores appeared on the film also. So, the specimens gained from 20% V/V ethanol were picked up to study more in R-SBF and scratch test in the further step.

4.3.1.3 Scratch test for scraped adhesion

After testing the film adhesion that gained from 20 % V/V ethanol electrolyte at -10 mA/cm^2 for 5 minute, the maximum applied load was 70g. After testing under load applied, the film still remained on substrates. Its shear stress, which determined by the equation from section 3.4.5, was 4.12 Mpa.



Figure 4.26 Scratch trace of as deposited film that gained from MCPM based 20% V/V ethanol electrolyte at -10 mA/cm^2 , 5 min deposition time.

4.3.2 After interval times in R-SBF

The selected specimen from above condition were soaked into R-SBF for 2, 4, and 8 hours respectively. The films surface observed by OM are as showed in figure 4.28.

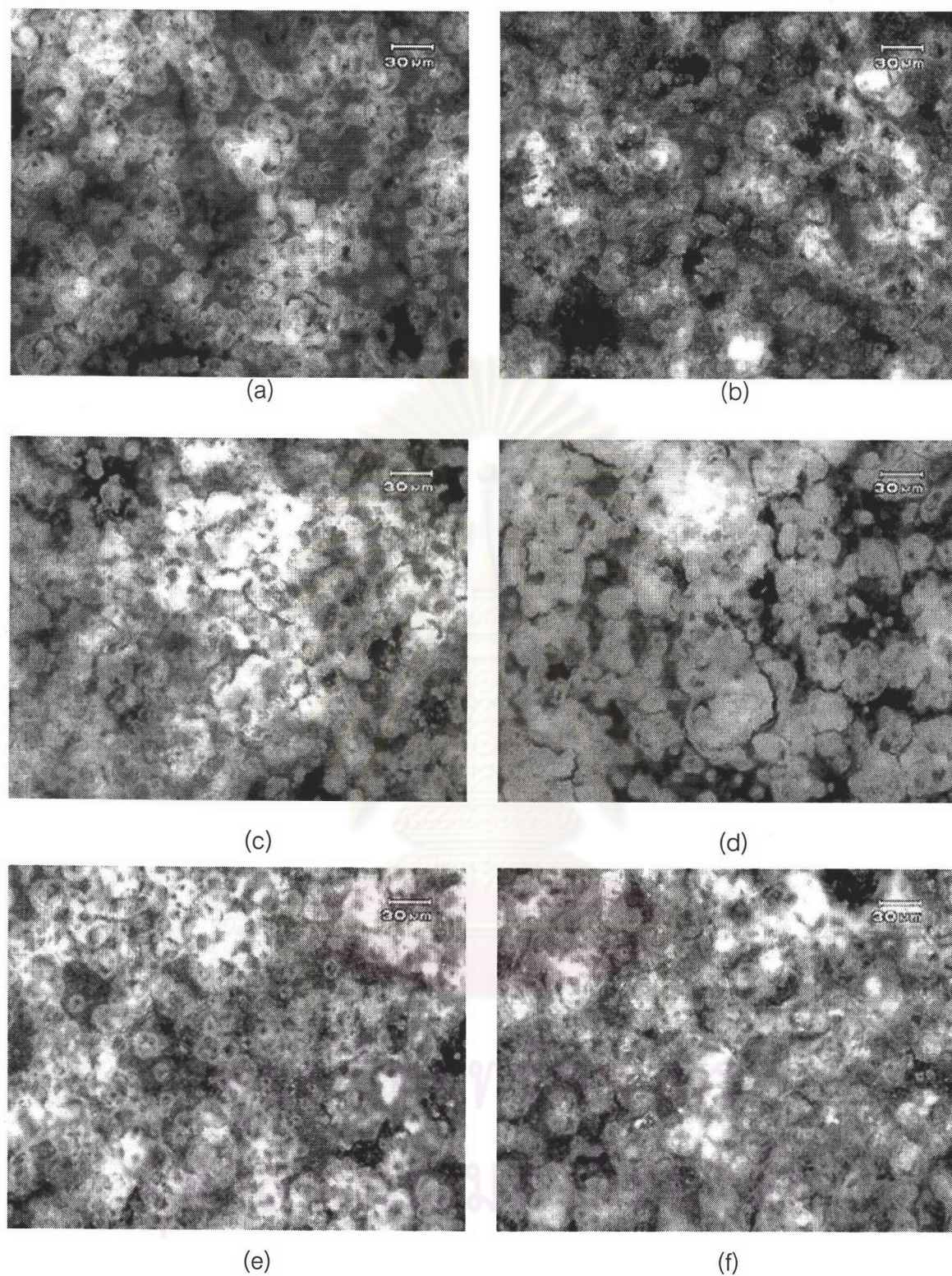


Figure 4.27 Optical micrographs of the films surface after soaking in R-SBF magnified at 200x, (a), (b), and (c) were the film surfaces at the deposition time for 3 mins subjected to R-SBF for 2, 4, and 8 hrs, respectively, (d), (e), and (f) were the film surfaces at the deposition time for 5 mins subjected to R-SBF for 2, 4, and 8 hrs, respectively.

4.3.2.1 X-ray Diffraction patterns

From optical micrographs (figure 4.27), it could be seen that the films were more porous surface. It might occur from some phases of the film were dissolved into R-SBF and not completely precipitated back to the films.

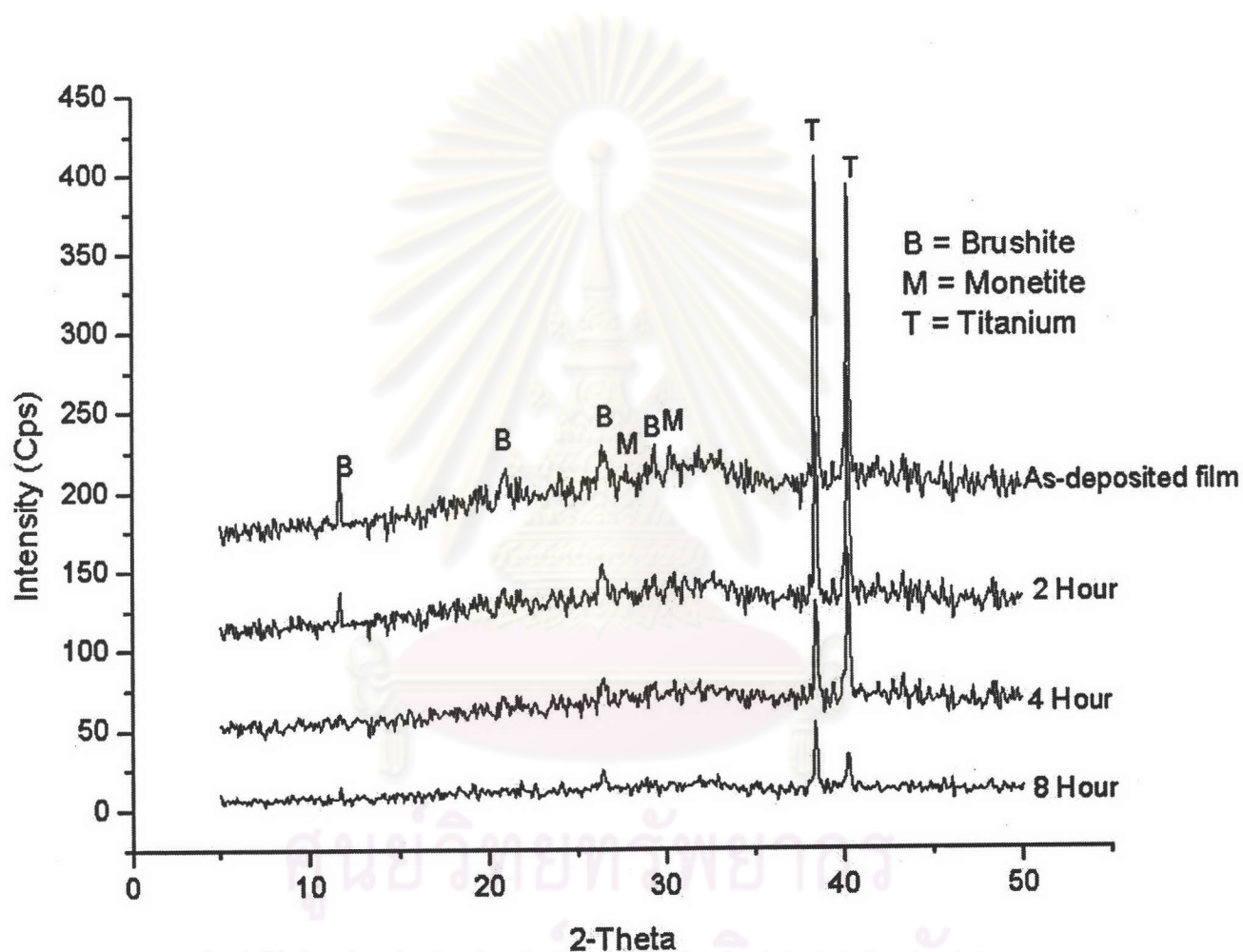


Figure 4.28 XRD patterns of the 3-mins as-deposited film from MCPM electrolyte based 20% V/V ethanol solution after soaking in R-SBF for 2, 4 and 8 hours.

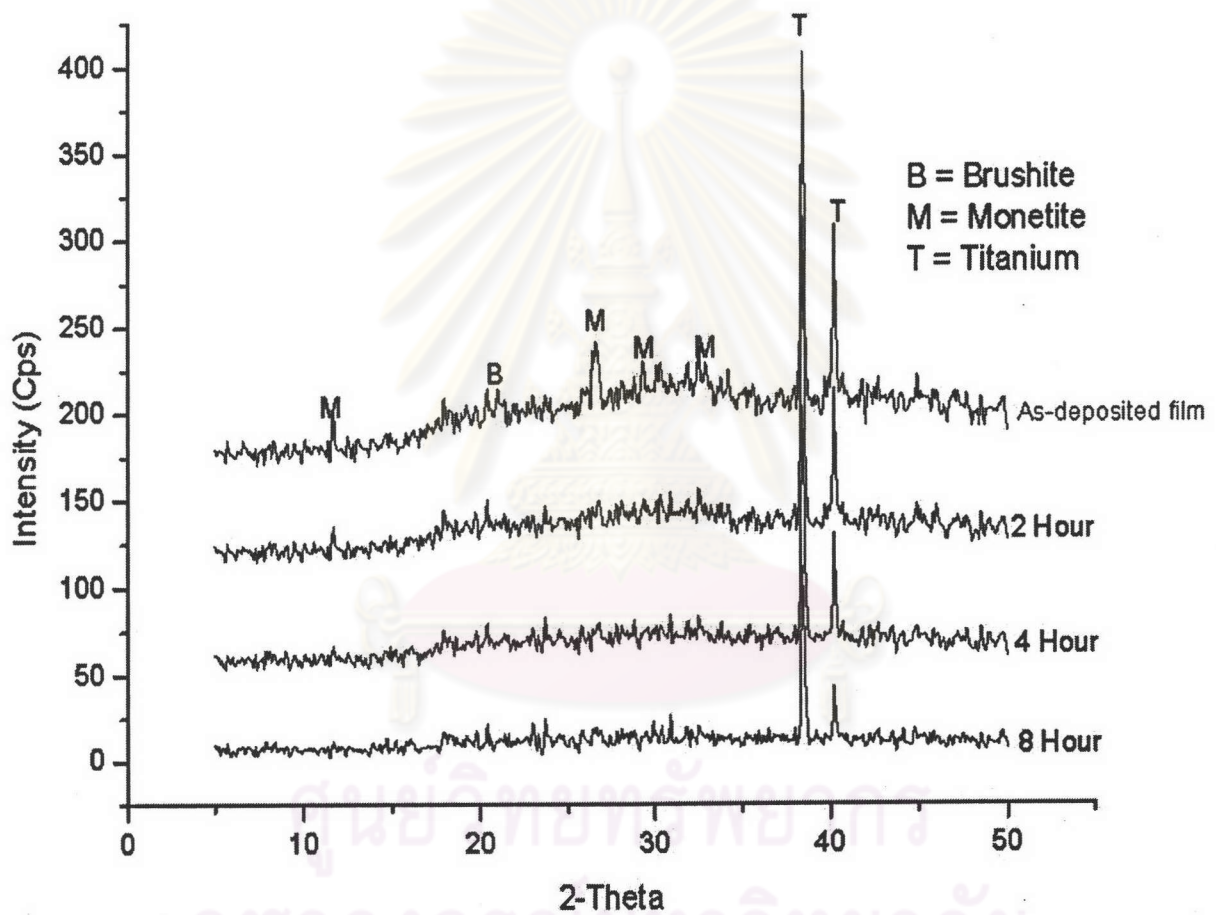


Figure 4.29 XRD patterns of the 5-mins as-deposited film from MCPM electrolyte based 20% V/V ethanol solution after soaking in R-SBF for 2, 4 and 8 hours.

4.3.2.2 Scanning electron microscope

SEM investigated the film microstructures after soaking in R-SBF for several interval times. Nevertheless, from its XRD results, peak intensity was decreasing with increasing of soaking time. Then, the film microstructure might be change during soaking process in R-SBF.

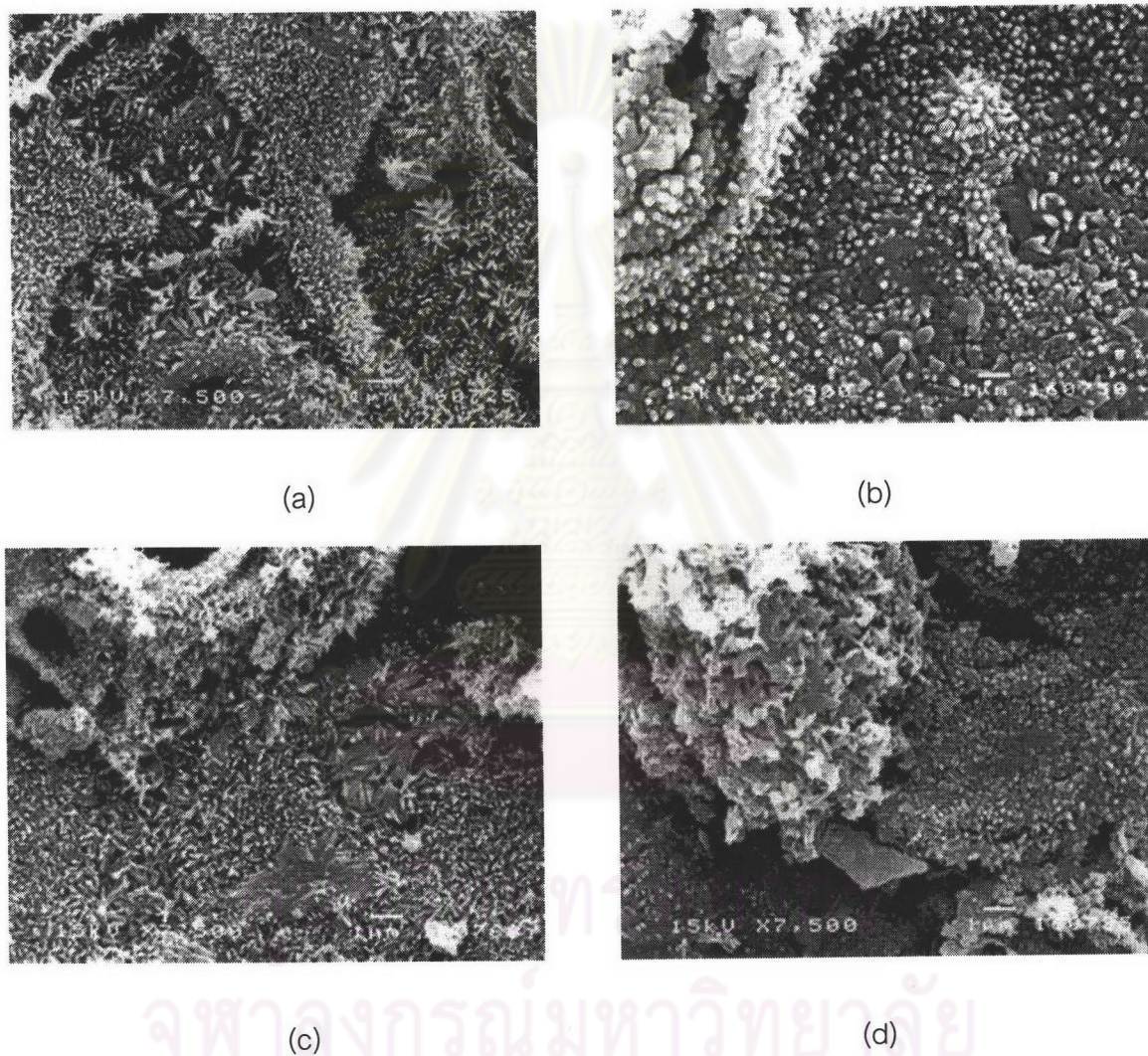


Figure 4.30 SEM micrographs of (a) the 3-min as deposited film from MCPM electrolyte based 20% V/V ethanol solution before soaking in R-SBF compared to the film after soaking in R-SBF for (b) 2 hrs, (c) 4 hrs, and (d) 8 hrs.

From figure 4.30, it could be seen that there were two phases existed in the film microstructure. A large amount of very fine crystal, this might be HAp, were covered

almost film surface^{*}. At figure 4.30(d) it still showed monetite phase with network structure. So, it could be say that the very fine primary crystal was deposited above other as-deposited phases.

According to XRD results of film characterization, the film gained from 5-mins of deposition time also showed the same results as the film gained from 3-min deposition time. Figure 4.31 showed the film microstructure at 5-mins of deposition time after soaking in R-SBF^{**}.

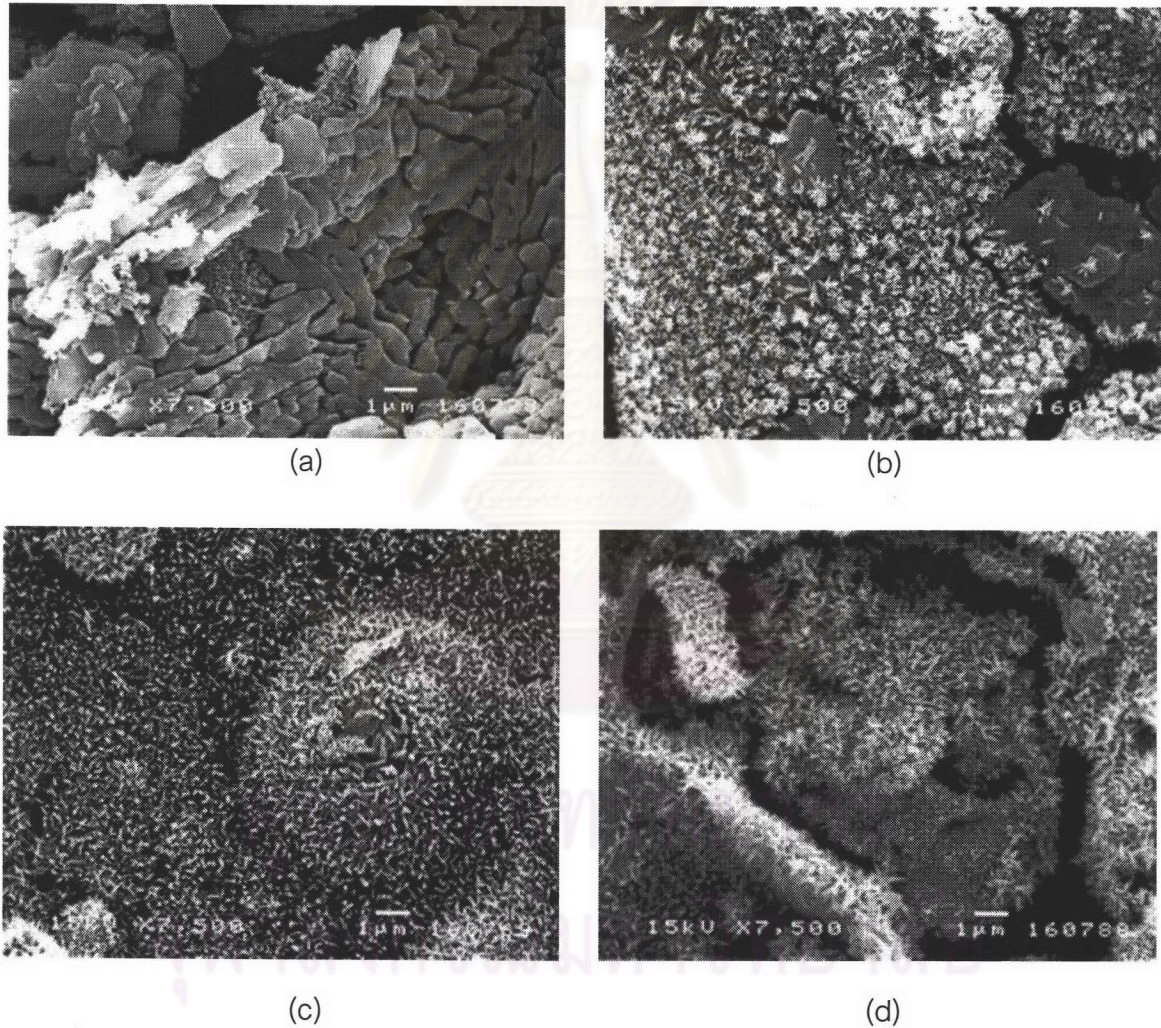


Figure 4.31 SEM micrographs of (a) the 5-min as deposited film from MCPM electrolyte based 20% V/V ethanol solution before soaking in R-SBF compared to the film after soaking in R-SBF for (b) 2 hrs, (c) 4 hrs, and (d) 8 hrs

* See Appendix H for more details.

** See Appendix I for more details.

4.4 DCPD electrolyte based 1M-H₃PO₄ solution.

4.4.1 As-deposited film

In this study, thin film of calcium phosphate were trying to form on titanium substrates. The optimum condition was established at -300mA/cm^2 for 7 and 10 minutes. The film surfaces when observed by OM were shown in figure 4.32.

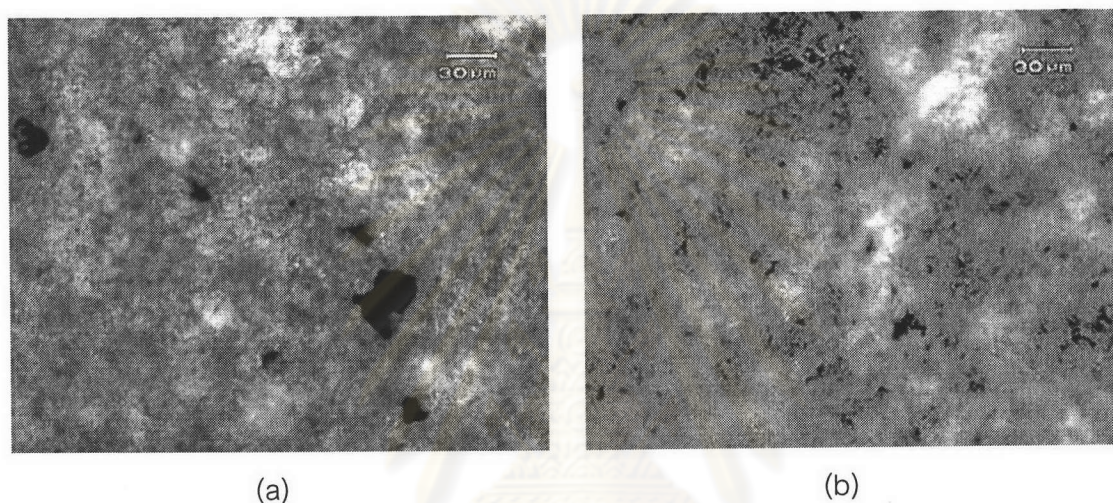
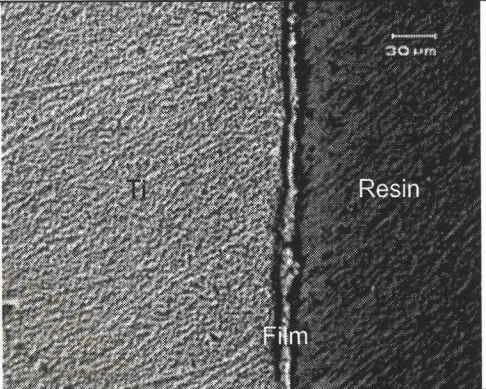
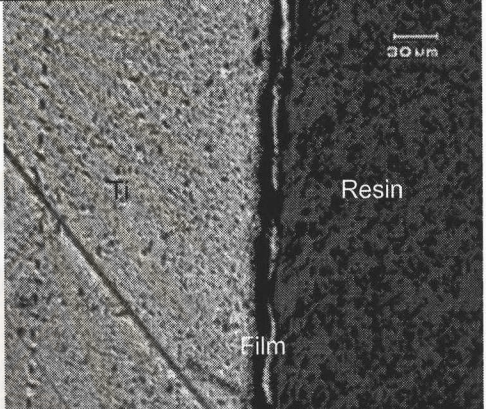


Figure 4.32 Optical micrographs of the film surfaces gained from DCPD electrolyte based 1M-H₃PO₄ solution at -300 mA/cm^2 at the depositon time of (a) 7 min and (b) 10 mins.

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Table 4.3 Film thickness gained from DCPD based 1M-H₃PO₄ electrolyte.

Conditions	Thickness	Photograph (200x)
7 min deposition time	8 μm	
10 min deposition time	10 μm	

From figure 4.32 and table 4.3, it was found that the obtained films were porous and quite thin when compared to previous electrolytes used in the experiment. XRD and SEM, however, characterized these specimens but it would not pick up for further scratch test and biomimetic study because of its very high current density for deposition.

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4.4.2 X-ray diffractometry pattern

Its XRD pattern was showed in the following figure 4.33.

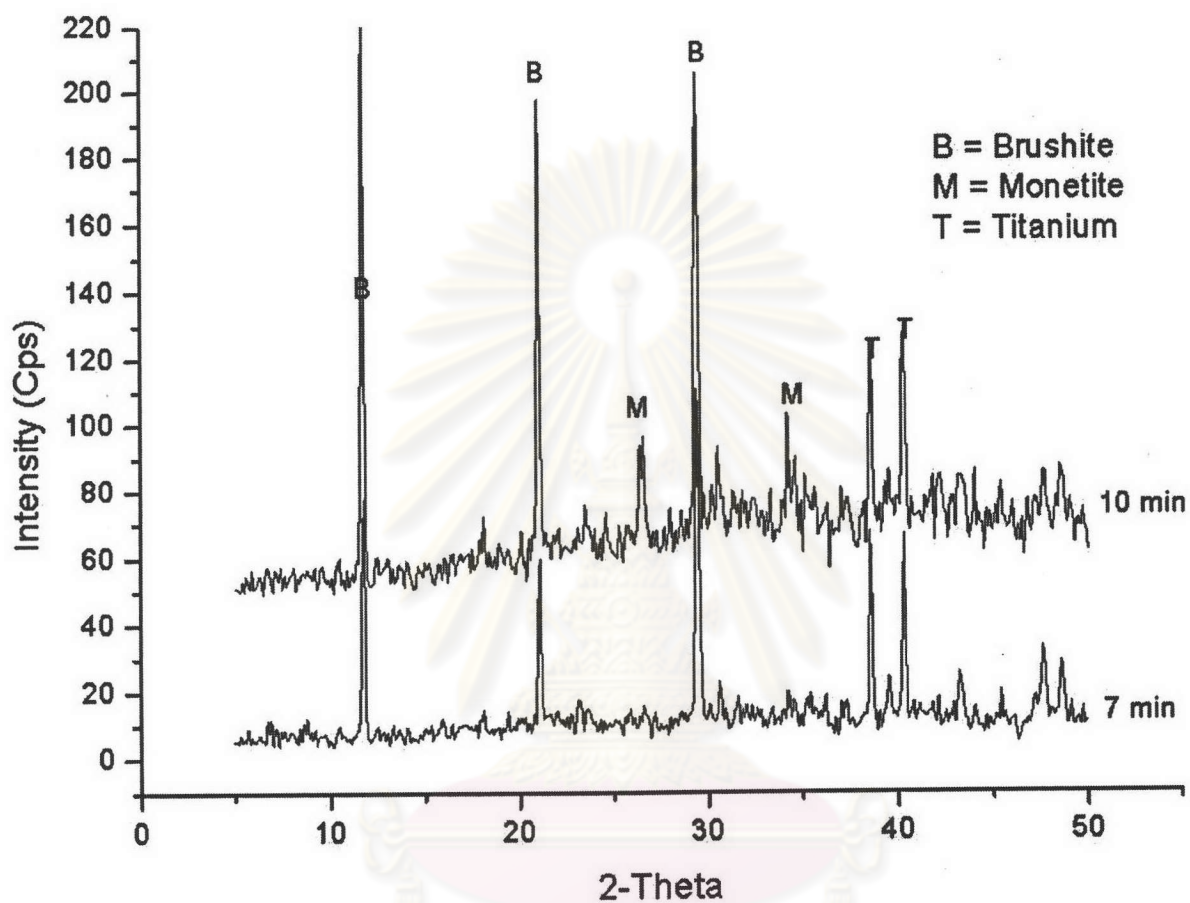


Figure 4.33 XRD pattern of the film gained from DCPD based $1\text{M-H}_3\text{PO}_4$ at 7 and 10 mins.

From XRD patterns, the existing phases were brushite and monetite for 10 mins of deposition time and the single phase of brushite was obtained at the deposition time of 7 mins.

4.4.3 Scanning electron microscope

Scanning electron microscope was used to investigate its microstructure of the film as shown in figure 4.34



Figure 4.34 SEM micrographs of the film microstructures gained from DCPD electrolyte based 1 M- H_3PO_4 solution at -300 mA/cm^2 for deposition time of (a) 7mins and (b) 10 mins.

From these above figures showed that brushite would appear as bigger primary crystals while smaller primary crystals were monetite.

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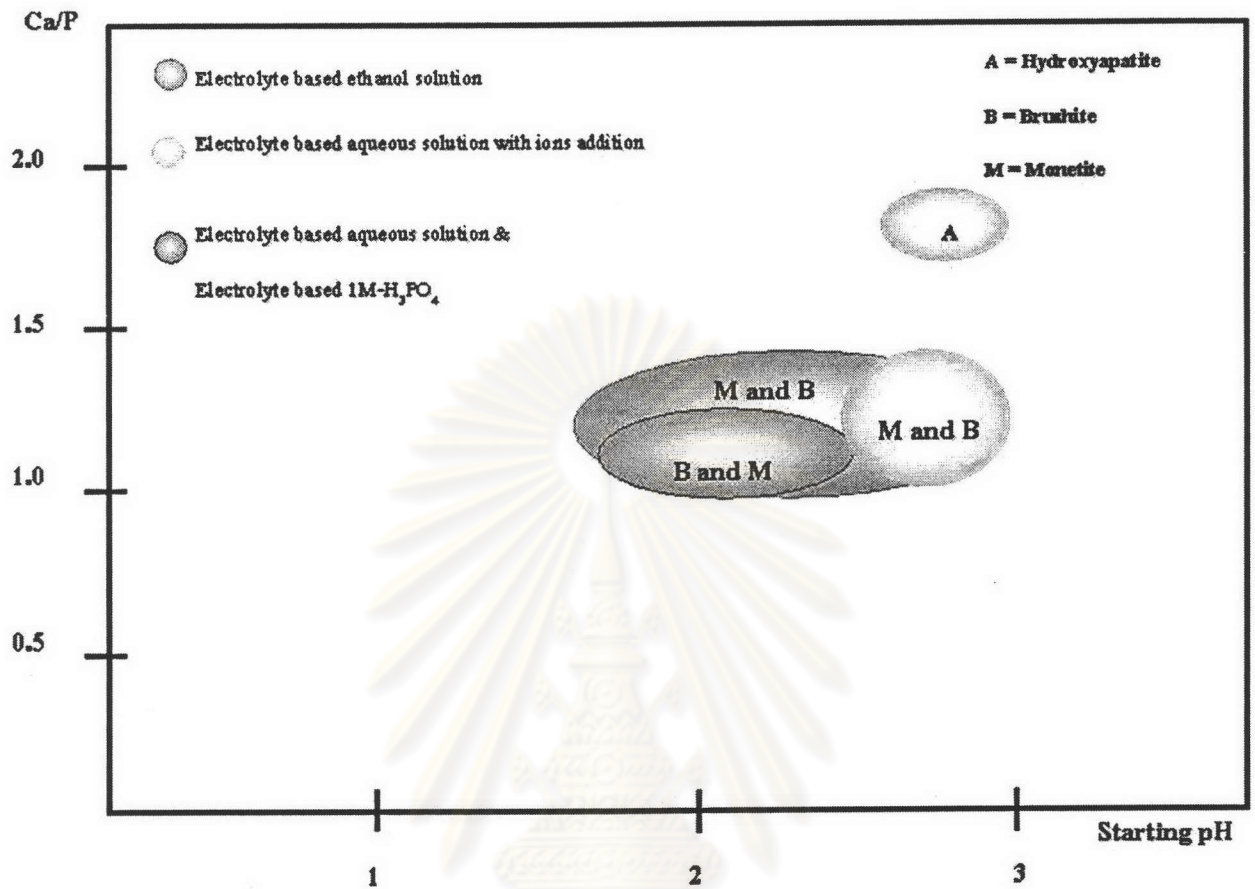


Figure 4.35 Schematic of Ca/P ratio of the obtained products in thin film correlated with electrolyte starting pH.

From Figure 4.35, it could be seen that brushite and monetite occurred in a wide region at pH 1.9 to 2.9. At pH 2.6 to 2.9, Hydroxyapatite could deposit in the film from MCPM electrolyte based aqueous solution with ions addition.

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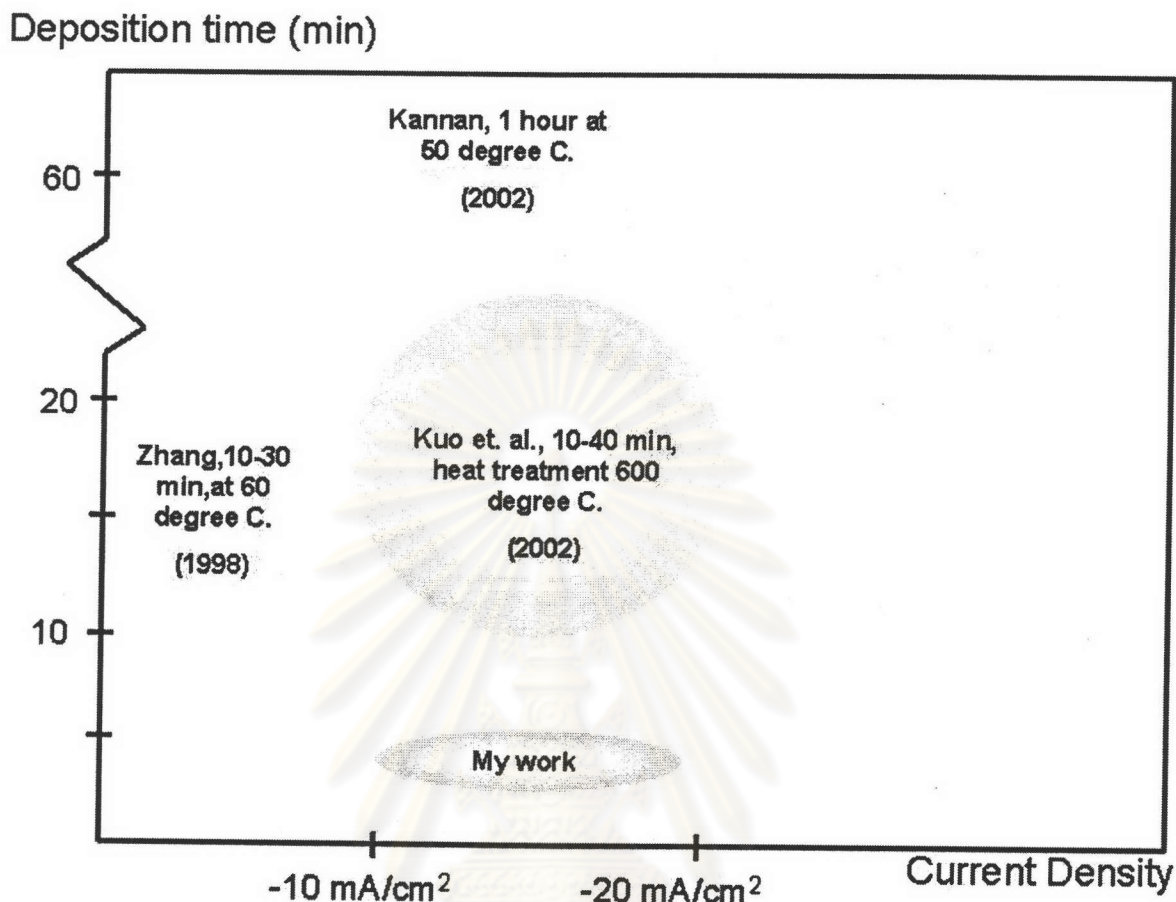


Figure 4.36 Schematic of the present work compared to previous works of other researchers.

From Figure 4.36, the schematic shows the present work when compared to the works of other researchers. Kuo[32] got hydroxyapatite film after 10-40 min deposited times in the range -10 mA/cm^2 to -20 mA/cm^2 and heat treatment at 600°C for 1 hour. Kannan[55] got hydroxyapatite film in the range -12 mA/cm^2 to -16 mA/cm^2 after 1 hour deposition time with elevated electrolyte temperature at 50°C . Zhang[31] also got hydroxyapatite film in the range -3 mA/cm^2 to -6 mA/cm^2 after 10-30 min deposition time with elevated electrolyte temperature at 60°C . For my work, the calcium phosphate film contained hydroxyapatite could deposited in the range -10 mA/cm^2 to -20 mA/cm^2 at 3-5 min deposition time at room temperature.