O U R N A L O F

Ceramic Processing Research

The effect of additives on the properties of HAp-Al₂O₃nano-composite powders

S. Tayebi^a, F. Mirjalili^b, H. Samadi^c and A. Nemati^d

^aDepartment of Materials Science and Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran

^bDepartment of Material Engineering, Maybod Branch, Islamic Azad University, Maybod, Iran

^cDepartment of Material Science & Engineering, Faculty of Engineering, Malayer University, Malayer, Iran

^dDepartment of Material Engineering, Sharif University, Tehran, Iran

Hydroxyapatite is the most important bio ceramic, due to its structure and chemical composition which is similar to bone. Since feeble fracture toughness, brittleness and low tensile strength have restricted their use, for overcoming this problem, they were often used as a secondary component. HAp-Al₂O₃ nano-composite powder combined the benefits of biocompatibility of HAp and high strength of Al₂O₃. When HAp-Al₂O₃nano-composite powders were sintered at a higher temperature than 1100-1200 °C, HAp was decomposed and converted to the second phase of TCP, due to the formation of calcium aluminate increasing decomposition speed of HAp to TCP at higher degree than 1100-1200 °C temperatures; therefore, with the addition of additives to the powders, the decomposition reaction of HAp could be inhibited and the properties could be improved. In this study the effects of alumina as reinforcement, pH, surfactant and different additives were investigated. At first, hydroxyapatite powder was synthesized. Then, the effect of different percentage of alumina (15, 20, 25), different pHs (9, 10, 11), different surfactants and different additives on HAp-Al₂O₃ nano-composite powder were studied. The results showed that the addition of different additives resulted in increase of the thermal stability and properties of HAp-Al₂O₃nano composite powder. By replacement of CΓ and F⁻ ions with OH⁻in HAp structure, decomposition of HAp decreased and stability of HAp at higher temperatures was increased. Owing to the decomposition of HAp, the reaction between CaO and Al₂O₃ reduced; therefore, the amount of calcium alumina phases decreased something which resulted in Al₂O₃ phase. Moreover, replacement of Cl⁻ and F⁻ ions in the apatite structure limited the growth of the grains and decreased the crystallinity that led to a better solubility and bioactivity behavior of nano composite powder.

Key words: Nano, Composite, HA, Alumina, Chemical precipitation.

Introduction

Since apatite-like structures have a hard tissue such as bones and teeth, Calcium phosphate is widely used in medicine [1]. Hydroxyapatite is calcium phosphate nearest to bone mineral and the most thermodynamically stable phase in the body [2]. Calcium phosphates, such as hydroxyapatite for their biocompatibility and similarity to the mineral components of bones and teeth are good replacements for parts of the body which are damaged [1]. Hydroxyapatite increases the capability of bone growth and forms a strong chemical bond with bone tissue when the bone tissue grows in the surface layer of this ceramic [3]. Nonetheless it is a brittle material which leads to low mechanical failure and limits its application in a position under the load. Therefore, it is important to add a secondary phase to improve the strength and mechanical properties of hydroxyapatite. The most important materials such as alumina, zirconia, titania and organic glass can be used as the reinforcing components [4].

Due to its unique thermal, mechanical, and chemical properties, alumina are applied widely in the strong materials, composites and reinforcing materials. Alumina as the engineering ceramic based on its high mechanical properties and biocompatible properties is used as bone and dental fittings [5-7]. Moreover, its application in biology increases owing to hardness, High strength against fatigue and resistance to corrosion [8].

The replacement of various ions such as sodium (Na), magnesium (Mg), fluorine (F), chlorine (Cl), aluminum (Al) improved chemical composition and structure of apatite. Ion substitution in the apatite structure not only leads to improving the biocompatibility, bioactivity, mechanical properties which are similar to the apatite body in terms of chemical composition, but also it decreased the therapy course and bone repair significantly [9-11].Therefore, in this research, the effect of additives such as NaF and MgCl₂.6H₂O on the HAp- Al₂O₃nano composite is investigated.

Experimental Activities

Preparation of nano hydroxyapatite powder

Nano crystalline hydroxyapatite particles were prepared by a solution-precipitation method using Ca $(NO_3)_24H_2O$

^{*}Corresponding author:

Tel : +0098-35-6235313

Fax: +0098-35-32370957

E-mail: fm.mirjalili@gmail.com

(Merck Prolabo 0308821 142) and $(NH_4)_2HPO_4$ (Merck Prolabo A0143307 037) as starting materials and ammonia solution as an agent for pH adjustment. A suspension of 0.4 M Ca $(NO_3)_24H_2O$ was vigorously stirred at 25 °C. A solution of 0.239 M $(NH_4)_2HPO_4$ was slowly added drop wise to the Ca $(NO_3)_24H_2O$ solution to obtain a Ca /P ratio of 1.67. The solution was stirred for 2 hrs and then was aged for 24 hrs. Following the separation of the deposition of the reaction solution, the solution was washed with distilled water and dried for 24 hrs at 110 °C. The final powders were calcined at 1200 °C for 1 hr.

Preparation of hydroxyapatite-Alumina nano composite powder

hydroxyapatite Nanocrystalline compounds were prepared by solution precipitation method using Ca (NO₃)₂4H₂O (Merck Prolabo 0308821 142) and (NH₄)₂HPO₄ (Merck Prolabo A0143307 037) as starting materials and ammonia solution as an agent for pH adjustment. A suspension of 0.4 M Ca (NO₃)₂4H₂O was vigorously stirred at 25 °C. After the preparation of 0.239 M (NH₄)₂HPO₄ solution, it was slowly added dropwise to Ca (NO₃)₂ 4H₂O solution; the resulting solution was mixed for 2 hrs (solution 1) and aged for 24 hrs. In the next step, Aluminum nitrate (LobaChemie 7784-27-2) was used as the starting material for the preparation of HA-Al₂O₃. Different amounts of Aluminum nitrate (15, 20, 25 wt %) were prepared in distilled water and mixed for 1 hr (solution 2) and aged for 24 hours. Then, the second solution with different weight ratios (15, 20, 25 wt %) was added to the first solution. The final solution was mixed for 2 hrs and aged for 24 hrs. After filtering, the materials were washed with distilled water and dried at 110 °C for 24 hrs and at last they was calcined at 1200 °C for 1 hr.

In the next part, for improving the properties, different additives were added. After ageing, the first and second solutions, Aliquat336 as a surfactant was added to the first solution, while the desired additives (MgCl₂.6H₂O and NaF) with weight percent of 5 and 10 wt% were added to the first solution. The final solution was mixed for 2 hrs and aged for 24 hrs. After filtering and washing, the materials were dried at 110 for 24 hours and were calcined at 1200 °C for 1 hr.

Phase identification was performed by X-ray diffraction (XRD) PW1800, of Philips Company, using nickel filtered Cu Ka radiation in the range of $2\theta = 10^{\circ}-60^{\circ}$ with a scanning speed of 5° per minute. Fourier transform infrared spectrometer (FTIR) by Perkin Elmer Spectrum 100 series was used with the universal attenuated total reflection (UATR) method. Microstructures of powders were identified by transmission electron microscope (Philips-Zeiss-Germany) and scanning electron microscopy (SEM Phenom).



Fig. 1. X-ray diffraction pattern of pure hydroxyapatite synthesized after calcination at 1200 °C for 1 hr.

Results and Discussion

Synthesis of nano crystalline hydroxyapatite powder The XRD peaks of hydroxyapatite powder after calcination at 1200 °C for 1 hr was illustrated in Fig. 1. The straight base line and sharp peaks of the diffractogram in Fig. 1 confirmed that the products were well crystallized. The XRD pattern in Fig. 1 indicated that the samples is mostly HAp. On the other side, another crystalline phase (tricalcium phosphate phase (TCP)) existed in the samples. The reactions involved in the formation of β -TCP during the chemical precipitation could be expressed as follows [12-14];

$$(Ca_{10}(PO_4)_6(OH)_2 \rightarrow 3Ca_3(PO_4)_2 + CaO + H_2O)$$
 (1)

The size of the crystalline was determined by the Scherrer method;

$$t = 0.89 \ \lambda \ / \ \beta \ \cos \theta \tag{2}$$

Where, t is grain size, θ is the wave length, λ is peak width chosen at half height in radians and β is the angle in degrees [15].

The crystallinity (Xc) of hydroxyapatite phase by X-ray diffraction patterns;

$$Xc = 1 - (V_{112/300} - I_{300})$$
(3)

Where, Xc is the degree of crystallinity of the powder, V_{112} / $_{300}$ the intensity of the cavity between the diffraction peaks (112) and I_{300} . [16, 17]

Accordingly, the degree of crystalline of pure hydroxyapatite was about 81.

Synthesis of hydroxyapatite-alumina nano composite powder

The XRD pattern of the pure hydroxyapatite (A), HAp-Al₂O₃ nano composite powder with 15% reinforcing alumina (B), HAp-Al₂O₃ nano composite powder with 20% reinforcing alumina (C) and HAp-Al₂O₃ nano composite powder with 25% reinforcing alumina (D) samples after calcination at 1200 temperature for 1 hr



Fig. 2. X-ray diffraction pattern of A, B, C and D samples after calcination at 1200 °C temperature for 1 hr.

Table 1. The size of the crystalline powder samples B, C and D.

5	I I ,
Sample	The size of the crystalline(nm)
В	61 nm
С	54 nm
D	35 nm
Table 2. comparing the crystaling	nity degree of samples B, C and D.
Sample	Degree of crystallinity

D	/ 1
С	71
D	60
were shown in Fig. 2. Con	nparing diffraction patterns of
the samples of A, B, C, D,	the formation of a TCP phase
could be accounted as the	main phase in the samples of
B, C, D. With increasin	ng alumina weight percent,
decomposition of HAp to	TCP phase increased and the
intensity peaks of hydroxy	apatite phase was decreased.

74

R

The absence of alumina phase peak was due to the reaction between CaO derived from hydroxyapatite analysis and Al_2O_3 and formation of $CaAl_2O_4$ phase which increased the degradation rate of hydroxyapatite phase. The reaction was shown as below:

$$nCaO + m Al_2O_3 \rightarrow Ca_nAl_{2m}O_{3m} + n$$
(4)

By increasing the amount of alumina, width peak of HAp was increased; therefore, the crystal size decreased [12-14, 18].

On the basis of Scherrer equation, the crystalline size of B, C and D samples after calcination at 1200 temperature for 1 hr was shown in Table 1.

The crystalline size of powders with increasing the alumina percent was decreased because the grain boundaries of alumina particles was prevented the growth of HAp.

The crystallinity degree of hydroxyapatite of B, C and D samples after calcination at 1200 °C temperature for 1 hr was shown in Table 2.



Fig. 3. X-ray diffraction pattern of the E, F and G samples after calcination at 1200 °C temperature for 1 hr.



Fig. 4. Graph of solubility versus pH.

The crystalline degree of apatite phase decreased with increasing the weight percentage of alumina while the decomposition of HAp to TCP phase increased; therefore, the intensity peak of hydroxyapatite phase decreased.

The effect of pH on hydroxyapatite-alumina nano composite powder

The XRD pattern of E (HAp-% $20Al_2O_3$ nano composite powder at pH = 9), F (HAp-% $20Al_2O_3$ nano composite powder at pH=10) and G (HAp-% $20Al_2O_3$ nano composite powder at pH = 11) after calcination at 1200 °C temperature for 1 hr was shown in Fig. 3. A comparison diffraction pattern of the E, F, G indicated that the formation of a TCP phase was the dominant phase in three diffraction patterns but with the pH decrease, decomposition of HAp to TCP phase increased, and the intensity peaks of hydroxyapatite phase decreased. The absence of alumina phase peaks was resulted from the reaction between CaO derived from analyses of hydroxyapatite and Al_2O_3 and formation of CaAl₄O₇, CaAl₂O₄ phases. The reaction was shown as below;

$$nCaO + m Al_2O_3 \rightarrow Ca_nAl_{2m}O_{3m} + n$$
(5)

The reaction between CaO and Al₂O₃phase led to the formation of calcium aluminate phase, and according to Le Chatelier's, it was responsible for increasing the degradation rate of hydroxyapatite phase. According to

Table 3. comparing the crysalinity size of samples E, F and G.

Sample	Crystalline size
PH = 9	40 nm
PH = 10	47 nm
PH = 11	54 nm

Table 4. The crystalinit	y degree of samples	E, F and G.
--------------------------	---------------------	-------------

Sample	(%)Crystalline degree
PH = 9	67
PH = 10	69
PH = 11	71

Fig. 4, lower pH increased the deposition of alumina and reaction between CaO, and Al_2O_3 phases which led to the formation of more calcium alumina phases [12-14, 18, 19].

The crystalline size of nano composites according to Scherrer method was shown in Table 3. It explained, that with pH increase, the crystalline size of powders increased and the decomposition of HAp decreased and consequently the reaction between CaO and Al_2O_3 reduced which reduces the amount of calcium alumina phases.With decreasing amount of calcium alumina phases, alumina could influence the grain boundaries and decreased the growth of the particles.

The crystalline degree of nano composite according to the method of Pang was shown in Table 4. It explained with pH increase, the crystalline degree of nano composite increased. It was due to the decrease in decomposition of HAp to TCP phase which led to the improvement of the intensity peaks of hydroxyapatite phase.

XRD results of HAp-%20Al₂O₃nano composite with different additives

Fig. 5 shows the XRD pattern of the HAp-%20Al₂O₃ nano composite powder without additives (sample H), HAp-%20Al₂O₃ nano composite powder with 5% additive MgCl₂.6H₂O (sample I) and HAp-%20Al₂O₃ nano composite powder with 10% additive MgCl₂.6H₂O (sample J) after calcination at 1200 °C temperature for 1 hr. Comparing the diffraction profile of samples show that the decomposition of HAp decreased, something which was due to the replacement of Cl⁻ to OH⁻ in HAp crystal. By increasing MgCl₂.6H₂O, decomposition of HAp decreased and stability of HAp at higher temperatures and intensity peaks of HAp phase were increased. Moreover, with increasing 10% of MgCl₂.6H₂O, decomposition of HAp decreased and reaction between CaO and Al2O3 increased something which led to reduction of the amount of calcium alumina phases and increase of Al₂O₃[12-14, 18, 20-22].



Fig. 5. X-ray diffraction patterns of H, I and J samples.

Table 5. The crystalline sizes of H, I and J samples.

Sample	Crystalline size
Sample H	54 nm
Sample I	44 nm
Sample J	41 nm

Table 6. The crystalline degree of H, I and J samples.

Sample	(%)Crystalline degree
Sample H	71
Sample I	73
Sample J	76

The crystalline sizes and crystalline degrees of HAp- $\%20Al_2O_3$ nano composite with different amount of MgCl₂.6H₂O were explained at Tables 5 and 6. As Table 5 and 6 indicate, by increasing the MgCl₂.6H₂O, the crystalline sizes were reduced and crystalline degrees of nanocomposites increased which was due to the replacement of Cl- to OH- in HAp crystal. By increasing MgCl₂.6H₂O, decomposition of HAp decreased; therefore, the intensity peaks of HAp phase increased.

Fig. 6 shows the XRD pattern of the HAp- $\%20Al_2O_3$ nano composite powder without additives(sample K), HAp- $\%20Al_2O_3$ nano composite powder with 5% additive NaF (sample L) and HAp- $\%20Al_2O_3$ nano composite powder with 10% additive NaF (sample M) after calcination at 1200 °C temperature for 1 hour.

Comparing the diffraction profile of samples shows that the decomposition of HAp decreased, which is due to the replacement of F^- to OH in HAp structure. By increasing NaF decomposition of HAp decreased and stability of HAp at higher temperatures and intensity peaks of HAp phase increased. Moreover with a 10% increase in NaF, decomposition of HAp decreased owing to the reaction between CaO and Al₂O₃that led



Fig. 6. X-ray diffraction patterns of H, L and M samples.

Table 7. Crystalline sizes of K, L and M samples.

Crystalline size	Sample
54 nm	K sample
41 nm	L sample
35 nm	M sample
Table 8. Comparing the crystalling	ne degree of K, L and M samples.
Sample	(%) Crystalline degree
K sample	71
L sample	81

to decreasing the amount of calcium alumina phases, thus the Al_2O_3 phase appeared [12-14, 18, 20-22].

84

M sample

The crystalline sizes and crystalline degrees of HAp-%20Al₂O₃ nano composite with different amount of NaF were show at Tables 7 and 8. As Tables 7 and 8 indicated, by increasing NaF, the crystalline sizes decreased and the crystalline degrees of nanocomposites increased something which was due to the replacement of F^- to OH^- in HAp crystal. By increasing NaF, decomposition of HAp decreased and an intensity peak of HAp phase was increased.

FTIR results of the HAp-Al₂O₃ nano composite

FTIR analysis of pure HAp was shown in Fig. 7. The FTIR shows the existence of phosphate (PO_4^{3-}) bonds at 570, 600, 950, and 1100-1090 cm⁻¹; hydroxyl (OH) bonds at 630 and 3567 cm⁻¹ and P-H band at 1989 and 2076 cm⁻¹ [23-30].

Structural changes at A, B, C; D samples were investigated by FTIR, which could be observed in Fig. 8. Metal-oxygen bond peak in the wave number of less than 500 cm⁻¹ was related to Al-O band. The peak marked with P-O was related to phosphate groups at crystalline hydroxyapatite network. Peaks appeared in



Fig. 7. FTIR curves of pure hydroxyapatite synthesized after calcination at 1200 $^{\circ}$ C for 1 hr.



Fig. 8. FTIR curves powder samples A, B, C and D.

 1800 cm^{-1} were related to the Al-O bond; therefore, with increasing weight percentage of alumina, the intensity peak of Al-O increased.

The peaks marked with P-H at wave numbers of 1989 cm^{-1} , 2076 cm⁻¹ and 12924 cm^{-1} were related to HPO_4^{-2} groups. The peak marked with H₂O belonged to the stretching vibration as well as the deformation vibration characteristics of hydroxylate O-H in the crystal lattice of hydroxyapatite, therefore with increasing weight percentage of alumina, the peak intensity of O-H decreased. The results of X-ray diffraction pattern and Pang calculations were confirmed this issue. The absence of peaks related to stretching structural hydroxyl groups and phosphate at the range of 630 cm^{-1} , 962 cm^{-1} indicated a decrease in the degree of crystallinity of hydroxyapatite phase of the composite sample compared to pure sample [18, 25-31].

Structural changes at E, F, G samples were investigated by FTIR which could be seen in Fig. 9. Metal-oxygen bond peak in the wave number of less than 500 cm⁻¹ related to Al-O bond. The peak marked with P-O was related to phosphate groups at crystalline hydroxyapatite network. Peaks appeared in 800 cm⁻¹ belonged to the Al-O bond stretching vibration therefore, with increasing deposition of alumina at lower pH, more calcium aluminate phases were formed. The peak was shown as O-H at 3572cm⁻¹ related to the deformation



Fig. 9. FTIR curves powder samples E, F and G.



Fig. 10. FTIR curves powder samples H, I and J.

vibration characteristics of hydroxylate O-H in the crystal lattice of hydroxyapatite [18, 23, 31].

Structural changes in powder samples H, I, J were investigated by FTIR which could be seen in Fig. 10. Metal-oxygen bond peak in the wave number of less than 500 cm⁻¹ was related to Al-O bond. The peak marked with P-O was related to phosphate groups at crystalline hydroxyapatite network. Peaks appeared in the wave numbers of 695 cm⁻¹ and 831cm⁻¹ at FT-IR spectrum of I and J samples were related to the stretching vibration of Mg-O-Al bond. Peaks appeared in 842 cm⁻¹ at FT-IR spectrum of I and H samples and peaks in the wave number of 831 cm⁻¹, 964 cm⁻¹ at FT-IR spectrum of sample J were belonged to the Al-O bond stretching vibration. With the addition of 10% MgCl₂.6H₂O at the wave number of 964 cm⁻¹, the peak related to Al₂O₃ phase appeared. Moreover, Peak marked with P-H at the area of 2924 cm⁻¹ in the spectrum of sample H and wave number of 1997 cm^{-1} at FT-IR spectrum samples of I and J were related to HPO₄⁻² groups. Consequently, with increasing deposition of alumina at lower pH, more calcium aluminate phases were formed. The peak shown with O-H which was related to the deformation vibration characteristics of



Fig. 11. FTIR curves of K, L and M samples.

hydroxyl O-H in the crystal lattice of hydroxyapatite [18, 20-28, 31].

FTIR spectrum of K, L, M samples were shown in Fig11. The same as previous spectrums, Metal-oxygen bond peak in the wave number of less than 500 cm⁻¹ was related to Al-O bond. The peak marked with P-O related to phosphate groups at crystalline hydroxyapatite network. Peaks appeared in the wave numbers of 827 cm⁻¹ at FT-IR spectrum of L sample and peak at 820 cm⁻¹ at FT-IR spectrum of sample M related to the stretching vibration of Al-F bond .Peaks appeared in 842 cm⁻¹ at FT-IR spectrum of K sample and peaks in the wave number of 960 cm⁻¹ at FT-IR spectrum of sample of M belonged to the Al-O bond stretching vibration. With addition of 10% NaF at the wave number of 960 cm⁻¹, the peak related to Al₂O₃ phase appeared. Moreover, Peak marked with P-H at the area of 2924 cm⁻¹ in the spectrum of sample K and wave number of 1993 cm⁻¹ at FT-IR spectrum samples of L and wave number of 2005 cm⁻¹ at FT-IR spectrum samples of M were related to HPO_4^{-2} groups. Therefore, with increasing deposition of alumina at lower pH, more calcium aluminate phases formed. The peak was shown as O-H mark related to the deformation vibration characteristics of hydroxyl O-H in the crystal lattice of hydroxyapatite. By increasing the percentage of NaF, the intensities of O-H peaks increased. The X-ray results and Pangs calculations confirmed above mentioned results [18, 22-27, 30, 31].

Morphological properties of the HAp-Al₂O₃nano composite

Fig. 12 shows the scanning electron microscopy (SEM) image of pure HA with good dispersion and regular shape. EDS results of sample A (pure HAp) is shown at Figure 12. The EDS results (part B) indicated the presence of calcium and phosphorus elements, and the weight ratio of calcium to phosphorus was 1.67, which was the ratio stoichiometry of apatite structure. The results of EDS map (Section C) established the uniform distribution of calcium and phosphorus of



Fig. 12. SEM image of sample A (part A), EDS results of sample A (part B), EDS map of sample A (part C).



Fig. 13. SEM image of sample C (A), EDS results of sample C(B), EDS map of sample C.



Fig. 14. SEM image of sample G (part A), EDS result of sample G (part B), EDS map of sample G (part C.

elements.

Fig. 13 shows SEM micrograph of sample C (HAp- $%20Al_2O_3$ nano composite powder). As it was shown, the grain growth of calcium alumina composition and their particle sizes increased at high temperatures. The results of EDS (part B) indicated the presence of calcium, phosphorus and alumina elements and the map of EDS (Section C) showed the uniform distribution of the elements.

Fig. 14 shows SEM image of sample G (HAp- $%20Al_2O_3$ nano composite powder at pH = 11). Porous appearances of nano composite with some agglomerations were shown clearly. Synthesized powder with some agglomeration inhabited the grain growth of particles at high temperatures. Very fine-grained spherical particles can be seen on the surface particle system. The results of EDS (part B) indicated the presence of calcium, phosphorus and aluminum elements. The results of EDS map (Section C) shows the uniform distribution of alumina in the composite field.

Fig. 15 shows sample I (HAp-%20Al₂O₃ nano

composite powder with 5% additive MgCl₂.6H₂O). Porous appearance indicated pirohydrolysis of magnesium chloride which resulted in the production of HCL gas that increased the pores and cracks in the surface of samples. Therefore, the ultrafine particles and active magnesium oxide could react with aluminum oxide and form the spinel. Very fine-grained spherical particles can be seen on the surface particle related to calcium aluminate compounds and spinel phases. Therefore it is evident that the addition of magnesium chloride led to the formation of spinel nanoparticles on the surface of particles. The result of EDS (part B) indicated the presence of calcium, phosphorus, aluminum and magnesium elements. The EDS map (Section C) shows the uniform distribution of alumina in the field of nano composite. By comparing Fig. 15 and 16, it was observed that by increasing magnesium chloride additives, the particle size decreased, and the uniform distribution of alumina at the field of nano composite would be spotted.

Fig. 17 shows sample L(HAp-%20Al₂O₃nano composite powder with 5% additive NaF) with Porous appearance



Fig. 15. SEM image of sample I (part A), EDS results of sample I (part B), EDS map of sample I (part C).



Fig. 16. SEM image of sample J (part A), EDS results of sample J (part B), EDS map of sample J (part C).



Fig. 17. SEM image of sample L (part A), EDS results of sample L (part B), EDS map of sample L (part C).



Fig. 18. SEM image of sample M (part A), EDS results of sample M (part B), EDS map of sample M (part C).

and spherical shape. EDS results (part B) indicated the presence of calcium, phosphorus, aluminum, and fluorine elements. The results of EDS map (Section C), shows the uniform distribution of alumina at the field of nano composite. By comparing Figs 17 and 18 it was observed that by increasing sodium fluoride additives, particle sizes became finer with regular shapes, due to

decreasing the grain size.

TEM images of samples C, G, J and M were used for investigating the particle size and morphology of nano composite powders. As Fig. 19 shows, the size of nanoparticles of sample C was about 50 nm with regular shape and some agglomeration. The particle size at sample G was about 50 nm with spherical shape The effect of additives on the properties of HAp-Al₂O₃nano-composite powders



Fig. 19. TEM images of sample C, sample G, sample J and sample M after calcination at 1200 °C temperature for 1 hr.

and a little agglomeration. In sample J, in the presence of surfactant and additive of MgCl₂.6H₂O, particles formed with the sizes less than 50 nanometers and regular geometric shape; however, they was some agglomeration. In samples M, in the presence of surfactants and additive of NaF, the particle size was about 30 nanometers with regular geometric shape and without any agglomeration. Therefore, it was concluded that the best sample was sample M with fine particles and spherical shapes without any agglomeration.

Conclusions

Nano HAp-%20Al₂O₃ nano composite powder with different additives was synthesized through precipitation method at 1200 °C. Under the conditions of precipitation techniques, with comparing different amounts of alumina (15, 20, 25%wt), the best value was obtained with 20% reinforcements of alumina. Formation of HAp-%20Al₂O₃nano composite powder was performed at different pH of 9,10,11 and the best value was at pH = 11. The formation of HAp- $%20Al_2O_3$ nano composite powder was achieved with 5% and 10% additives of MgCl₂.6H₂O and NaF and the best value obtained with10% additives. By replacing F⁻ and Cl⁻ ions after adding of 10% additives of MgCl₂.6H₂O and NaF, decomposition oFHAp reduced and thermal stability at higher temperatures increased. By increasing 10% NaF as an additive and surfactant, the particle size of nano composite became about 30 nm with regular shape and good dispersion.

References

 A.I, Misions, T.C, Vaimakis and C.C Trapalis, J.Ceramic international 6 (2010) 623-637.

- 2. F.N.J. Okatar, Materials letters60 (2006) 2207-2210.
- 3. R.T. Franceschi and B.S. Lyer, Bone Mineral Research 7 (1992) 235-246.
- 4. J.C. Zurita, D. Bermu and I. Lopez-Valero, Biomaterials Butter Worth (1994) 267-271.
- R. Vaben and D. Stover, Journal of Material Processing Technology 92 (1999) 84-90.
- N. Bahlawane and T. Watanabe, Journal of American Ceramic Society 9 (2000) 2324-2326.
- 7. L.A. Xue and I.W. Chen, Journal of Material Science 11(1992) 443-445.
- E.L. Andi, S. Sprio, M. Sandri, A. Tampieri, L. Bertinetti and G. Martra. Key Engineering Mmaterial (Bioceramics) 20 (2008) 171-174.
- 9. H. Eslami, M. Solati-Hashjin and M. Tahriri, Material Science and Engineering 29 (2009) 1387-1398.
- H. Eslami, M. Solati-Hashjin and M. Tahriri , Journal of Ceramic Processing Research 9 (2008) 224-229.
- 11. C. Ergun, Z. Evis, T.J. Webster et. al, Ceramics international 37 (2011) 971-977.
- 12. H. Ji and M. Marquis, Biomaterials 13 (1992) 744-748.
- B.D. Cullity, Addison-wesley Series in Metallurgy and Materials, United States (1978) 281-290.
- Y. X. Pang and X. Bao, Journal of the European Ceramic Society 23 (2003) 1697-1704.
- E. Landi, A. Tampieri and G. Celotti, Journal of the European Ceramic Society 20 (2000) 2377-2387.
- 16. X. Du, Y. Wang and J. Li, Powder Technology 192 (2009) 40-46.
- I. Kutbay, B. Yilmaz and Z. Evis, Ceramics International 40 (2014) 14817-14826.
- Z. Evis and R. Doremus, Materials Research Bulletin 43 (2008) 2643-2651.
- 19. J. Tossell, American Mineralogist 84 (1999) 1641-1649.
- D. Gopi, M. Thameem Ansari and E. Shinyjoy, Spectro Chemical Acta A 87 (2012) 245-250.
- 21. S. Pramanik, I. Agarwal and K.N. Rai, Trends in Biomaterials 19 (2005) 46-51.
- A. Sobczak-kuupiec, D. Malina and R. Kijkowska, Digest Journal of Nano materials and Biostructures 7 (2012) 385-390.
- 23. A. Balamurugan, S. Kannan and S. Rajeswari, Trends in Biomaterials 16 (2002)18-20.
- S. Mondal, B. Mondal and A. Dey, Journal of Minerals and Materials Characterization and Engineering 11 (2012) 55-67.
- 25. M. Sadat-Sojae, Journal of The Iranian Chemical Society 6 (2009) 386-392.
- 26. H. Chen and B.H. Clarkson, Journal of Colloid and Interface Science 288(2005) 97-103.
- 27. Y. Han, K. Xu, G. Montay, T. Fu and J. Lu, Journal of Biomedical Materials Research 60 (2002) 511-516.
- 28. S. Alamolhoda, S.S. Ebrahimi and A. Badiei, Iranian International Journal of Science 5 (2004) 31-42.
- 29. Y. Sung and D. Kim, Journal of Crystal Growth 254 (2003) 411-417.
- S. Kim, H. Bang, J. Song and S. Park, Ceramics International 35 (2009) 1647-1650.
- 31. Z. Evis and R. Doremus, Materials Research Bulletin 43 (2008) 2643-2651.