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PREPARATION AND CHARACTERIZATION OF CALCIUM HYDROXYAPATITE

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SUMMARY

Hydroxyapatite, $Ca_5(PO_4)_3OH$ was prepared via the reaction of calcium hydroxide with orthophosphoric acid or between calcium nitrate and diammonium hydrogen phosphate at different pH 's and temperatures of aging. The crystalline phases were detected by XRD. The molar Ca / P ratio was found to be approximately 1.72. The specific surface areas m^2/g were also calculated. The Transmittance Electron Microscope, (TEM) indicate that the hydroxyapatite powder (HA) produced was prismatic in shape with uniform size. The IR spectra of the prepared powder were given. The solubility of the synthesized powder, bulk density in g/cm^3 , water abrorption % and apparent porosity % were also given. The Scanning Electron Microscope, (SEM) shows the agglometration in the grains and its fine nature.

Keywords: HA,β – TCP, TEM and SEM.

INTRODUCTION

Hydroxyapatite (HA) is an attractive material for bone and tooth implantation because of its physical and chemical properties. Research work was carried out for the application of HA in the form of powder or granules or processed plugs as root filling [1]. Several attempsts were made to produce HA in the form of plugs alone and with mixtures of calcium hydroxide and calcium carbonate to be used as root canal fillings instead of Gutta Percha [2,3].. Also, in operative dentistry, it could find its application in tooth restoration with laser treatments [4,5]. There are several ways for HA preparation. The first procedure was carried out by Jarcho et al. [6],, in which they prepare HA via addition of $(NH_4)_2HPO_4$ to a solution of $Ca(NO_3)_2$.

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The second procedure was suggested by Osaka et al. [7] and Slosarczyk et al. [8]. They recommended the reaction between $Ca(OH)_2$ and H_3PO_4 or $(NH_4)_2HPO_4$. The aim of this work is to select the optimum method of preparation hydroxyapatite by characterizing the produced crystalline phases.

Results and Discussion

Chemical Analysis

The synthesized powders were found free from CaO, whatever pH or temperature of aging. In all cases the Ca/P ratio* was found to be around 1.72.

X-Ray diffraction analysis (XRD)

The XRD patterns of synthesized HA are present in **Fig.(1-6)** and the identified crystalline phases detected are shown in **Table (1).**

Table (1): Phases identified by XRD.

Sample	**Before heat treatment**	After heat treatment
A-1	$HA + \beta - Ca_3(PO_4)_2$ (Whitlochite)+$CaCO_3$ (Aragonite)+$Ca_3(PO_4)_2$. nH_2O (Calcium phosphate Hydrate)+$Ca_2P_2O_7$. $4H_2O$) (Calcium phosphate Hydrate) sys-orhorhombic)	$HA + \beta - Ca_3(PO_4)_2$
A-2	$HA + \beta - Ca_3(PO_4)_2$ +$CaCO_3$(Aragonite) + $Ca_3(PO_4)_2.4H_2O$) (Calcium phosphate Hydrate)	$HA + \beta - Ca_3(PO_4)_2$
A-3	HA	HA
A-3a	HA	HA
A-3b	HA	$HA + \beta - Ca_3(PO_4)_2$

* The calcium and phosphorus percentages were determined using atomic absorpiton spectra.

The reaction between $Ca(OH)_2$ and $(NH_4)_2HPO_4$ at pH 6 (Sample-A-1) give minor amounts of three different phosphate phases beside aragonite and HA. These phases readily gave HA and β- Tricalcium phosphate (β-TCP) on heat treatment at 1200 ^{0}C, **Fig. (1).**

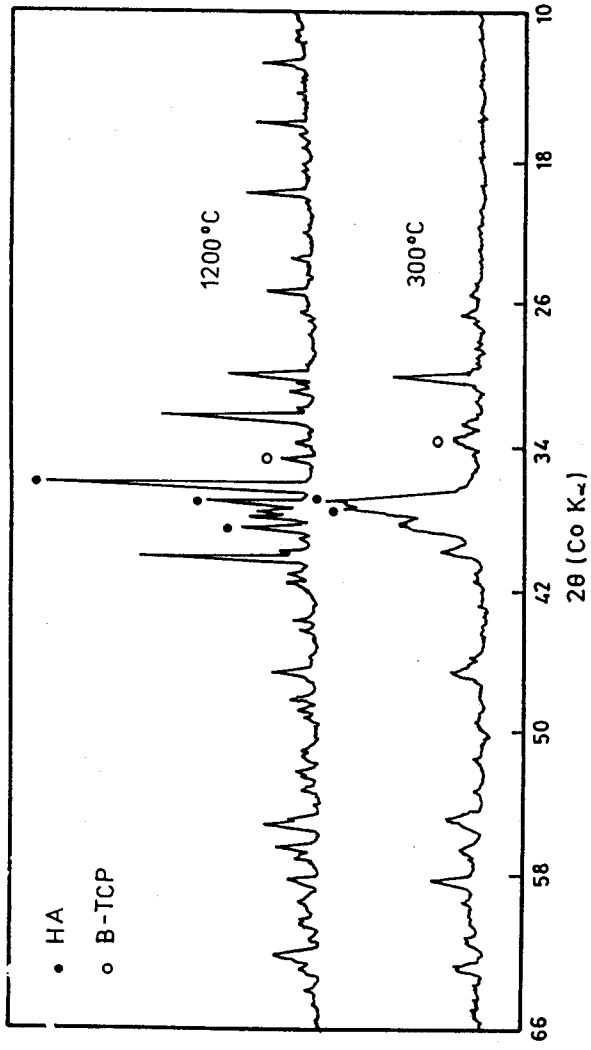

Fig. (1): XRD Patterns of A-1 Fired at 300° and 1200° C

Raising pH to 8(sample A-2) caused the disappearence of $Ca_2P_2O_7$ but HA was associated with aragonite and $\beta-TCP$ where, they gave HA and $\beta-TCP$ at 1200 ^{0}C, **Fig.(2).**

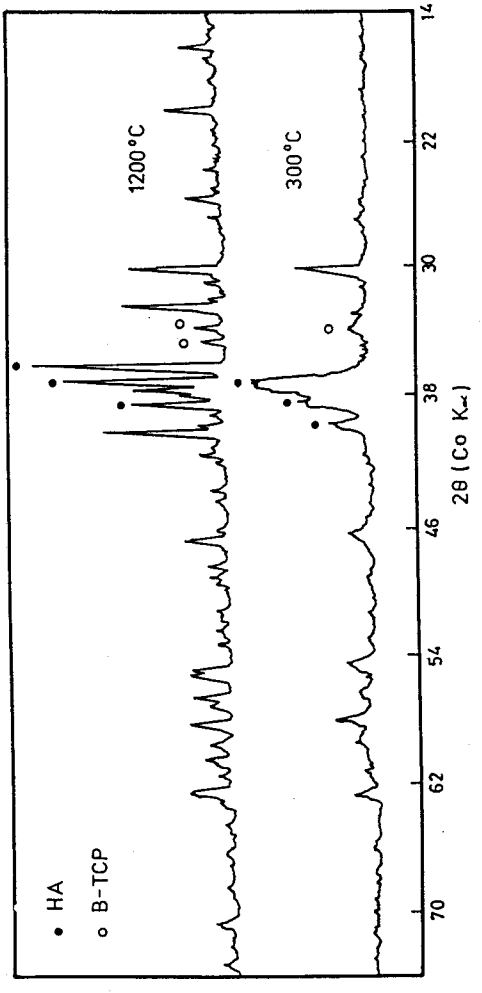

Fig. (2): XRD Patterns of A-2 Fired at 300° and 1200° C

Aging the precipitated powder, results from the reaction between $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$, at 23^{0}C (sample A-3a), 65^{0}C (sample A-3) and 95 ^{0}C (sample A-3b)

gave one phase of HA at 23^0C and 65^0C before and after heat treatment **Figs.(3,4),** while the powder aged at 95 ^{0}C gave β – TCP beside HA after heat treatment.

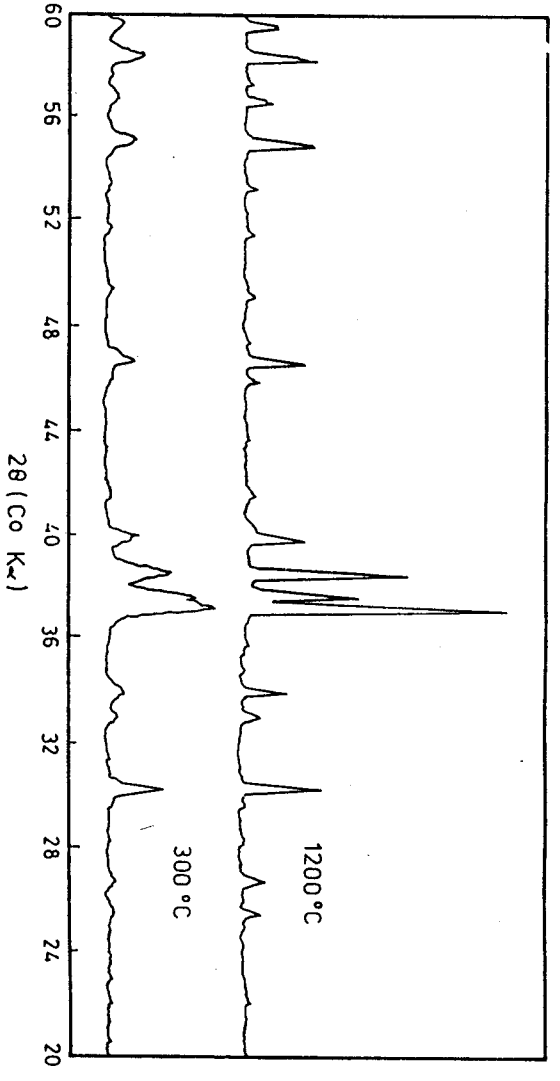

Fig. (3): XRD Patterns of A-3 Fired at 300° and 1200° C

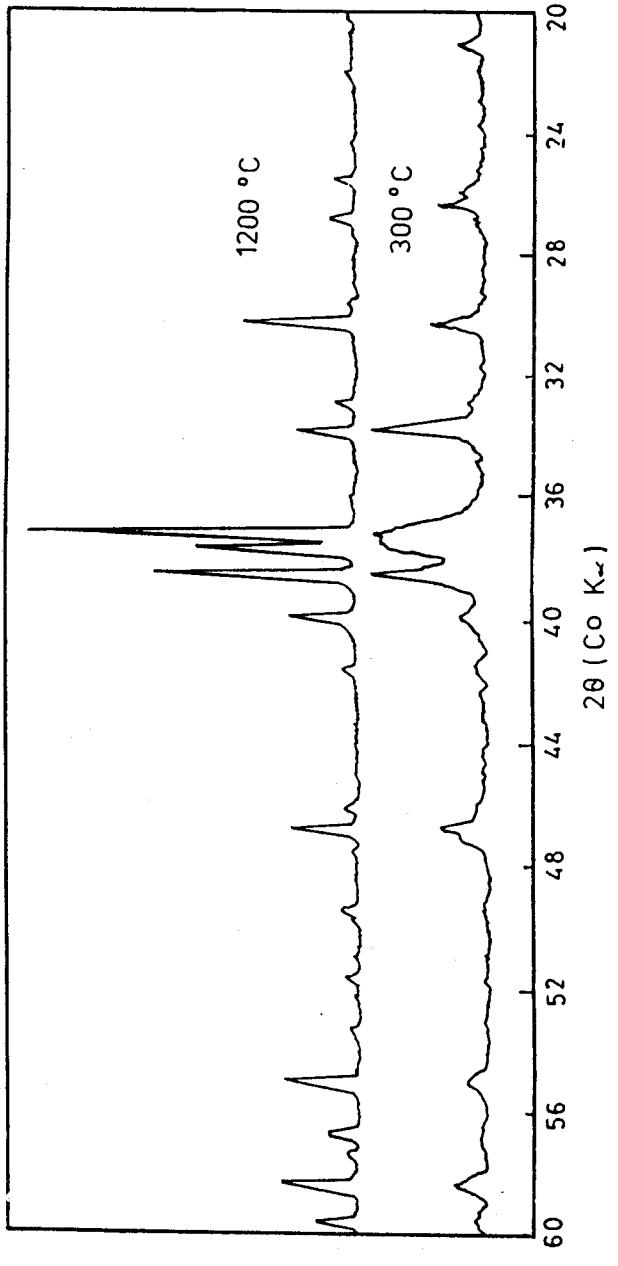

Fig. (4): XRD Patterns of A-3-a Fired at 300° and 1200° C

All hydrothermally treated powders gave HA alone even that aged at 95 ^{0}C **Fig. (5).**

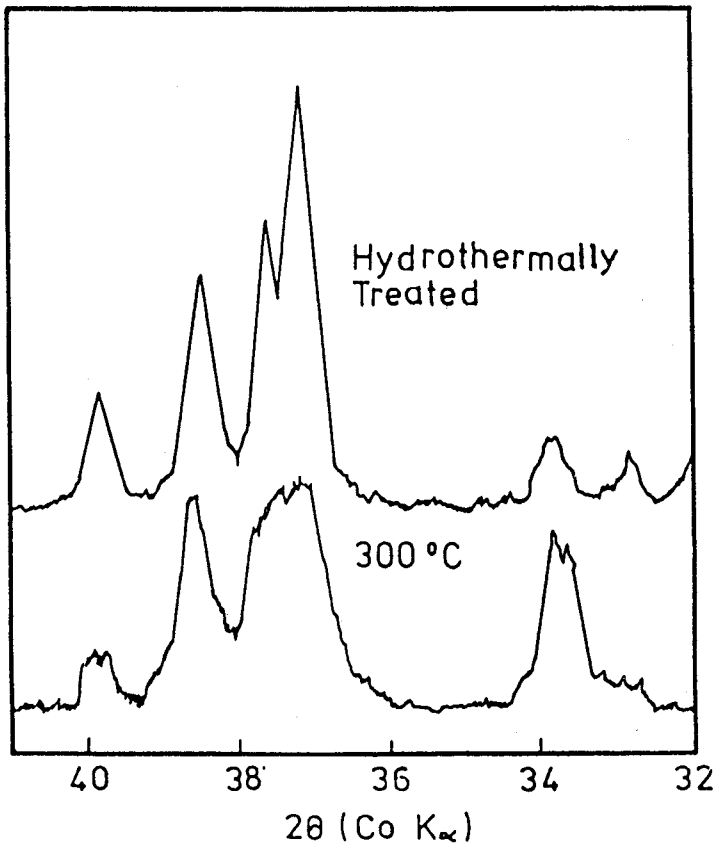

Fig. (5): XRD Patterns of A-3 Fired at 300° C and Hydrothermally Treated at 350° C

HA powder synthesized from $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$ (sample A-3) at pH 11 and 65 ^{0}C was treated at different temperatures in range between 300 to 1200 ^{0}C. XRD patterns obtained are shown in **Fig.(6).**

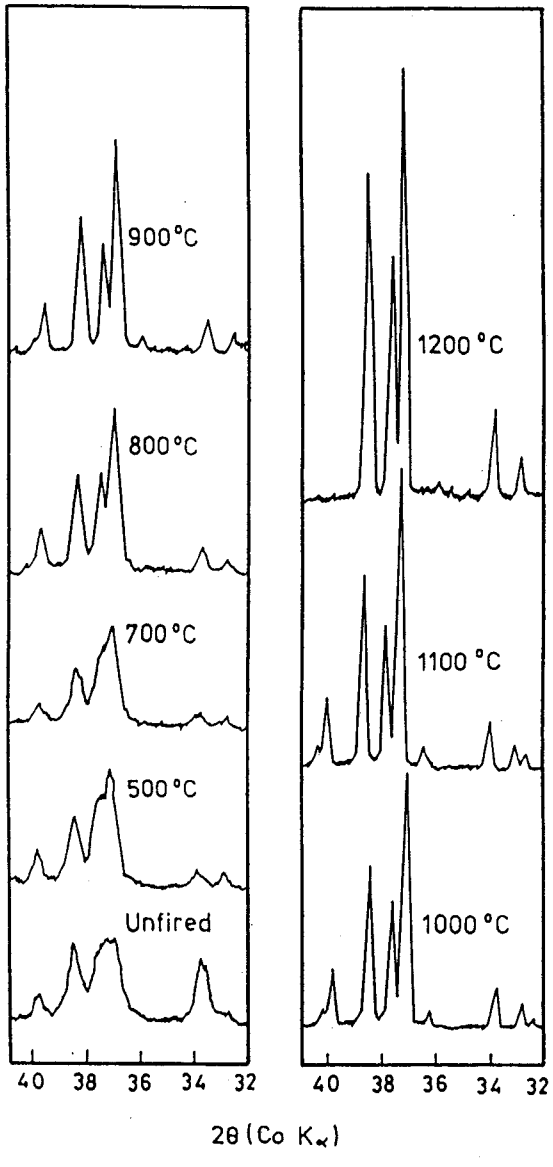

Fig. (6): XRD Patterns of A-3 at Different Temperatures

The results reveal that from 300 to 800 ^{0}C and at 1200^{0}C HA exist in pure phase, while partial dissociation into β-TCP and HA was detected at 900, 1000 and

1100 ^{0}C. **Table (2)** shows the results of particle size of HA powders calculated from XRD patterns.

Table (2): The particle size of HA fired at different temperatures. Where A-3=HA at pH 11, temperature 65 ^{0}C.

Sample	(D) –A^0	Calculated sp. Sr. A.
A-3 → 300^{0}C	851.69	223.21
A-3 → 500^{0}C	890.40	213.51
A-3 → 700^{0}C	932.91	203.78
A-3 → 800^{0}C	1400.71	135.72
A-3 → 900^{0}C	1957.28	97.13
A-3 → 1000^{0}C	1959.39	97.02
A-3 → 1200^{0}C	1961.54	96.92

Specific Surface area

The measured values of specific surface area shown in **Table (3)** are less than those calculated from XRD broading technique, here too, apecific surface area was affected by precursors, temperature of aging and temperature of calcination. Hydrothemal treatment at 200 and 350 ^{0}C cause a growth in particle size.

Table (3): Determination of specific surface area, BET-c constant and total pore volumes for samples as obtained from nitrogen adsorption

Sample	$S_{BET}m^2/g$	$S_t m^2/g$	BET-C Constant	Vp (total pore volume) (m^2/g)
A-3a(un fired)	162.65	168	15	0.510
A-3a(Fired at 1200^{0}C)	88.40	74	2	0.082
A-3 at 300^{0}C	123.37	124	18	0.456
A-3 at 500^{0}C	92.07	98	17	0.399
A-3 at 800^{0}C	79.54	75	5	0.171
A-3 at 1200^{0}C	72.65	70	4	0.095
A-3 aut. 200^{0}C	95.15	94	19	0.316
A-3 aut. 350^{0}C	94.80	92	19	0.323

Transmittance Electron Microscope (TEM)

* The calcium and phosphorous percentages were determined using atomic absorption spectra.

The TEM of the synthesized HA powders demonstrated in **Fig. (7)** indicate that HA produced powder is prismatic in shape with uniform size occurring in clusters segregated together with platy shaped particles appeared in powders synthesized at low pH.

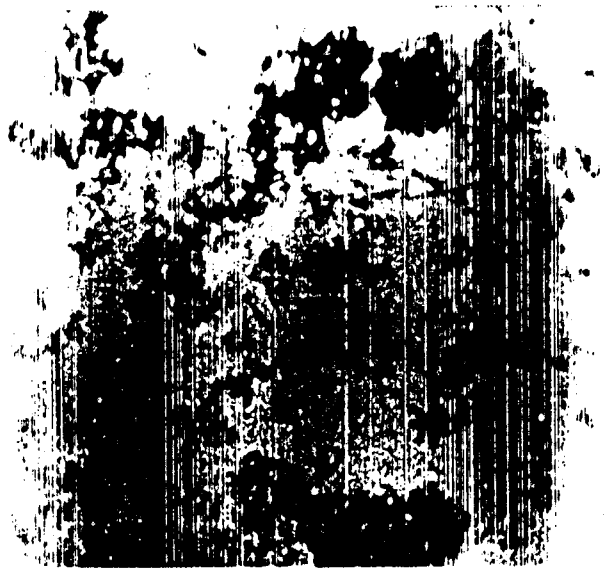

Fig. (7): TEM. of A-3 Fired at 300° C

Infrared Spctrophotometry

The infrared spectral patterns of prepared powder from $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$ (sample A-3) at pH 11, 65 ^{0}C and fired at 300 and 1200 ^{0}C are shown in **Fig. (8)** When this powder is hydrothermally treated at 200 and 350 ^{0}C, the IR spectral patterns are shown in **Fig. (9).**

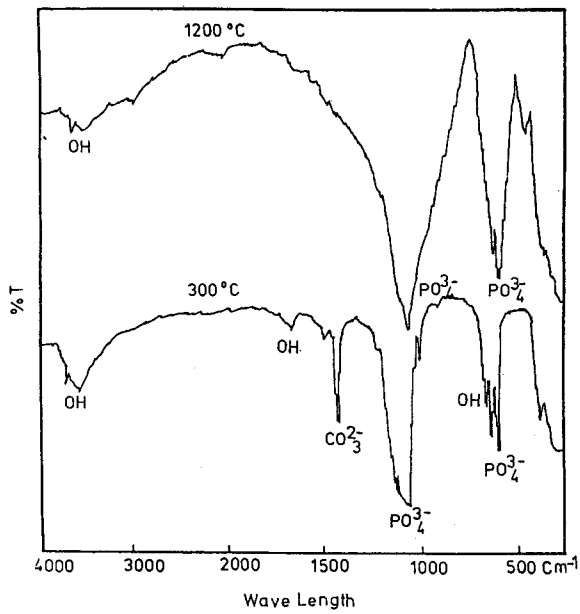

Fig. (8): IR Spectral Patterns of A-3 Fired at 300° and 1200° C

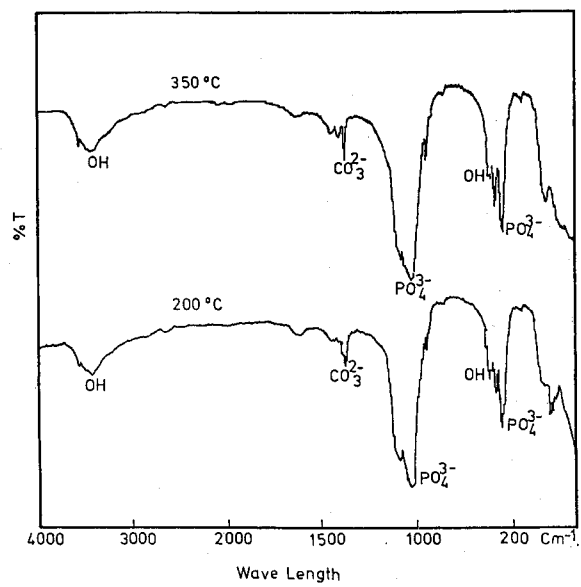

Fig. (9): IR Spectral Patterns of A-3 Hydrothermally Treated at 200° and 350° C

Physical Properties

The results of physical properties in terms of bulk density, water absorption and apparent porosity of HA prepared at pH 11, temperature 65 ^{0}C and fired at different temperatures are shown in **Table (4).**

Table (4): Physical properties of synthesized HA, powder fired at different temperatures.

Sample	Bulk density g/cm^3	Water absorption %	Apparent porosity %
A-3 at 300^{0}C	1.39	38.59	53.64
A-3 at 500^{0}C	1.43	37.58	53.74
A-3 at 700^{0}C	1.45	36.45	52.85
A-3 at 800^{0}C	1.46	35.41	51.69
A-3 at 900^{0}C	1.53	33.68	51.53
A-3 at 1000^{0}C	1.79	24.25	43.40
A-3 at 1000^{0}C	2.27	12.46	28.28
A-3 at 1000^{0}C	2.78	4.09	11.37

Where A-3=HA at pH 11 and temperature 65^{0}C.

Solubility of Synthesized HA Powder

The powders synthesized at pH 6 or 8 were slightly more soluble than those synthesized at pH 11. Also aging at low temperature of 23 ^{0}C raised the solubility from 0.4 to 0.8 $\mu g/cm^3$.

Calcination temperature of synthesized HA affected the degree of solubility of the powder.

Scanning Electron Microscope (SEM)

The SEM shows the agglomeration of the grains and its considerably fine nature. It is evident from **Fig. (10),** the presence of open pore system in-between the agglomerates which is clear in the fractured surface.

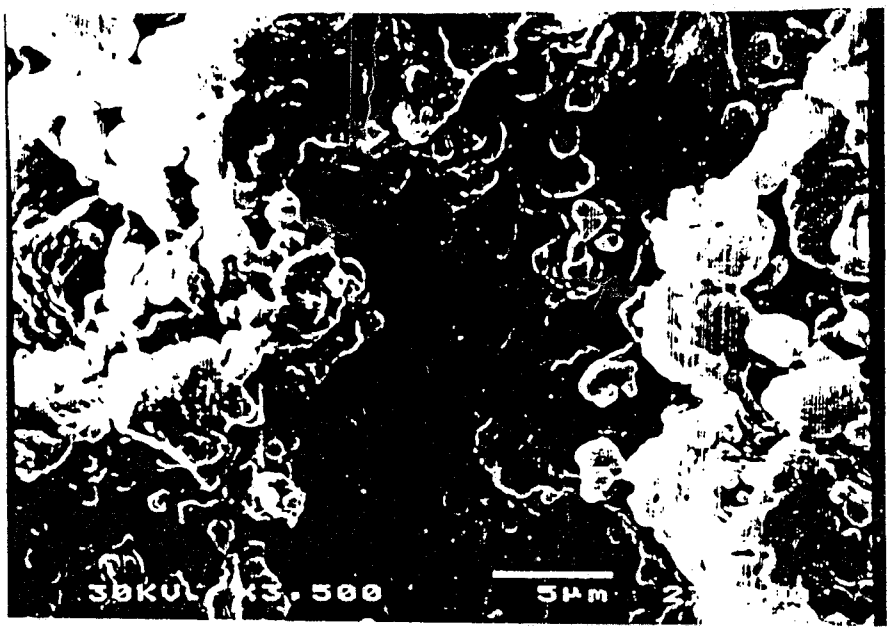

Fig. (10): SEM of fractured surface of unfired A-3 processed under 10 KN. Fired at 1200° C × 3500

Experimental

HA is firstly prepared from the reaction between calcium hydroxide and orthophosphoric acid according to the equation,

$5\,Ca(OH)_2 + 3H_3PO_4 \rightarrow Ca_5(PO_4)_3OH + 9H_2O$

Procedure

Chemical Preparation

0.1M Calcium hydroxide is dispersed in 200 cm^3 distilled water. While vigorous stirring, 200 cm^3 of 0.3M orthophosphoric acid solution is added dropwise within 0.5.h and with rate of addition of 10 cm^3 /sec.

The pH is adjusted at 8.00 with ammonia solution. The developed suspension is heated under reflux at 65 ^0C for 20 min. The experiment is repeated at pH 6.0 to study the effect of pH.

The second method for preparation of HA is by the reaction of $Ca(NO_3)_2.4H_2O$ with $(NH_4)_2HPO_4$ at pH (11-12).

Separate aliquots of $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$ solutions are prepared by dissolution of $Ca(NO_3)_2$ (1.0M) in 100 cm^3 distilled water and $(NH_4)_2HPO_4$ (0.6) in

100 cm^3 distilled water, the pH's of both solution are adjusted at 11 using ammonia solution. The phosphate solution is added dropwise to the nitrate solution over period of 0.5h., while stirring. The milky gelatinous perecipitate is left to digest under reflux at 65 ^{0}C for 1.0h. with continuous stirring. The precipitate is thoroughly washed and separated by centrifuging. The effect of temperature during the digestion process on the powder produced is studied by carrying the preparation at different temperatures mainly, 23, 65 and 95 ^{0}C.

The prepared hydoxyapatite undergo hydorthermal treatment at 200 and 350^{0}C and also thermally treated at 1200 ^{0}C for 2.0h. X-ray diffraction is carried out not only to identify the phases but also to evaluate the average particle size (D) by the use of sherrer formula.

$$D = 0.9/B\cos.\theta$$

The prepared (HA) from different routes are characterized in terms of determination of Ca/P ratio, crystalline phase, surface area, grain size, IR spectrographic analysis, morphology and size of grains of prepared powder by transmission electron microscope, sinterability of the powder, scanning electron microscope and solubility of the (HA) powder.

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