

# Structural, Morphological and Physical Properties of TiH<sub>2</sub> Incorporated Hydroxyapatite

**Nanthini Amirthalingam**

Anna University Chennai

**Sathishkumar Panchatcharam**

Anna University Chennai

**THENMUHIL Deivarajan** (✉ [thenmuhil@annauniv.edu](mailto:thenmuhil@annauniv.edu))

Anna University Chennai <https://orcid.org/0000-0002-0809-6196>

**Manohar Paramasivam**

Anna University Chennai

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## Research Article

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## Cover letter

May 30, 2021

Editorial Department of Journal of Advanced Ceramics  
Tsinghua University Press  
B605D, Xue Yan Building, Beijing 100084, China

Dear Editor of Journal of Advanced Ceramics

I am submitting a manuscript for consideration of publication in Journal of Advanced Ceramics. The manuscript is entitled “Structural, Morphological and physical properties of TiH<sub>2</sub> incorporated Hydroxyapatite”.

It has not been published elsewhere and that it has not been submitted simultaneously for publication elsewhere.

Titanium incorporated Hydroxyapatite preparation was endeavored using TiH<sub>2</sub>. The hydroxyapatite (HAp) was obtained from wet chemical facile method and was mixed with TiH<sub>2</sub> (5 to 20%). The mixes were shaped by pressing and samples were sintered at different temperatures from 900°C to 1200°C. The experimental result from XRD clearly reveals that the product composition leads to TCP and CaTiO<sub>3</sub> major phases. SEM results showed that grain size increased at 1200°C with increase in wt % of TiH<sub>2</sub>. The outcome of the sintering studies carried out shows that the maximum porosity was obtained at 5wt% of TiH<sub>2</sub> addition with the HAp at sintering temperatures of 900°C and 1000°C. The incidence of broad sintering reactions and phase dissociation of HAp leads to development of TCP–CaTiO<sub>3</sub> composites.

Thank you very much for your consideration.

Yours Sincerely,

Dr. Thenmuhil Deivarajan

Anna University

Chennai – 600 025

Tel.: 044 2235 9200

E-mail: [thenmuhil@annauniv.edu](mailto:thenmuhil@annauniv.edu)

# Structural, Morphological and physical properties of TiH<sub>2</sub> incorporated Hydroxyapatite

Nanthini Amirthalingam<sup>a</sup>, Sathishkumar Panchatcharam<sup>a</sup>, Thenmuhil Deivarajan<sup>a,\*</sup>, Manohar Paramasivam<sup>a</sup>

<sup>a</sup> Department of Ceramic Technology, Alagappa College of Technology, Anna University,  
Chennai 600 025.

Authors Email Id: [nanthini2k@gmail.com](mailto:nanthini2k@gmail.com), [passathis@gmail.com](mailto:passathis@gmail.com), [pmano@annauniv.edu](mailto:pmano@annauniv.edu)

Corresponding Authors Email: [\\*thenmuhil@annauniv.edu](mailto:thenmuhil@annauniv.edu)

Tel: 044 2235 9200.

## Abstract

Titanium incorporated hydroxyapatite preparation was endeavored using TiH<sub>2</sub>. Titanium has good mechanical properties, good biocompatibility and bioactivity. Titanium incorporated hydroxyapatite material prepared for orthopedic applications were reported to be better mechanical properties. Hydroxyapatite (HAp) was synthesized by wet chemical facile method and after calcination was mixed with TiH<sub>2</sub> (5 to 20%). The effect of sintering on phase formation, microstructure, density and porosity of Hap/TiH<sub>2</sub> was studied by sintering at temperatures from 900°C to 1200°C. The properties of the samples were characterized using X-ray diffraction technique (XRD), Scanning electron microscopy (SEM), Fourier transform spectroscopy (FT-IR), density and porosity. The results from studies showed the presence of  $\beta$ -tricalcium phosphate ( $\beta$ -TCP) and perovskite (CaTiO<sub>3</sub>) as the major crystalline phases; while minor reaction products like  $\alpha$ -TCP and TTCP were also recorded for samples with higher amount of TiH<sub>2</sub> irrespective of sintering temperatures. Morphology evaluation by SEM revealed the presence of CaTiO<sub>3</sub> needle

structure at temperature till 1000°C, above which it appeared hexagonal due to crystal growth. Functional groups, density and porosity were also studied.

*Keywords: Hydroxyapatite; Perovskite; Microstructures; Sintering; porosity*

## **1.Introduction**

Hydroxyapatite (HAp) is composed of a network of calcium orthophosphates and is widely used in biomedical applications like orthopedics and dentistry as it is similar to the mineral component of bone and teeth. HAp is water-insoluble, biodegradable and bioactive since after some time it is partially resorbed and replaced by natural bone [1]. HAp has been used in various bone repair and replacement applications in the form of dense or porous blocks, granules, powders, coatings or as a mineral component in a polymer composite [2]. HAp can be synthesized by different routes such as solid-state reaction, sol-gel process, hydrothermal process, micro emulsion technique, precipitation process, biomimetic process, etc. Among these methods, chemical precipitation is the widely used method as it is economical and provides pure product.

Natural bone and teeth are porous materials which have porosity in micrometer range. Sponge bone has 50 to 90% porosity with pore diameter of roughly 1  $\mu\text{m}$  [3, 4]. Even the Haversian canals in cortical bone contain 3 to 12% porosity [5]. In teeth, the open porosity of the dental tissue ranges between 1.11% and 3.08% of its volume [6]. In bone tissue engineering, a scaffolding material is utilized either to actuate the development of bone from the encompassing tissue or to go about as a bearer or template for implanted bone cells or agents [7].

Porous structures and rough surfaces are essential for encouraging bone ingrowth and osteointegration, which makes dense HAp less resorbable and osteoconductive compared to porous HAp for the healing/filling of osseous defects. For obtaining cell migration and transportation of nutrients and metabolic wastes, highly porous architecture with interconnected porous network is important [8,9].

Porous material can be prepared by sacrificial template process[10,11,13] gel casting of foams [12], powder metallurgy [14], freeze drying [15] etc. All these methods result in porous structure with different pore characteristics. General pore creating materials are naphthalene, hydrogen peroxide and other similar materials which are easily vaporizable. In this work,  $\text{TiH}_2$  in various amounts is added to HAp and characterized to investigate its ability to act as pore former due to the presence of hydrogen group. Further, the incorporation of titanium ion with HAp to form composite is investigated.

Titanium and its alloys have been widely utilized as metallic implant materials because of the blend of advantageous properties like good mechanical properties, good biocompatibility and bioinertness. F.N. Oktar studied the mechanical properties of  $\text{TiO}_2$  (5 to 10wt %) added to HAp with different sintering temperatures between 1000 and 1300°C [17].

Research was earlier done on sintered density and microstructure modifications on the usage of  $\text{TiH}_2$  powders along with Ti. When  $\text{TiH}_2$  powder was used as an alternative starting material to Ti metal powder in titanium sponge preparation, it gives the benefit of reduced cost in titanium powder metallurgy since  $\text{TiH}_2$  is a transitional product in the hydrogenation - dehydrogenate (HDH) operation[18-19].  $\text{TiH}_2$  particles are most encouraging than the pure Ti

Particles because of the sintering behavior of  $\text{TiH}_2$  [20]. Previously,  $\text{TiH}_2$  powders were used to enhance the foaming process of Titanium scaffolds in orthopedic applications [21].

The decomposition of the hydride is belated when  $\text{TiH}_2$  powder is pre-treated in atmospheric air condition at certain temperature [23]. The dehydrogenation of  $\text{TiH}_2$  occurs in a two-step process given as  $\text{TiH}_2 \rightarrow \text{TiH}_x \rightarrow \alpha\text{-Ti}$ , where  $0.7 < x < 1.1$  [24]. The coloration of  $\text{TiH}_2$  powder is the easiest way to estimate the stage of oxidation during the dehydrogenation of  $\text{TiH}_2$ . During heat treatment, the black powder turned to olive green at  $400^\circ\text{C}$ , purple at  $450^\circ\text{C}$  and blue between  $500^\circ\text{C}$  and  $550^\circ\text{C}$  [22].

The purpose of this novel work is to prepare composites with synthetic HAp and  $\text{TiH}_2$ , and to analyze whether  $\text{TiH}_2$  had functioned as a pore former or an additive or both. 5 – 20wt. % of  $\text{TiH}_2$  was added to HAp and sintered at  $900^\circ\text{C}$  -  $1200^\circ\text{C}$  in pressureless sintering to study the effect of sintering temperature on phase formation, microstructure, functional group formation, density and porosity of samples with different  $\text{TiH}_2$  content.

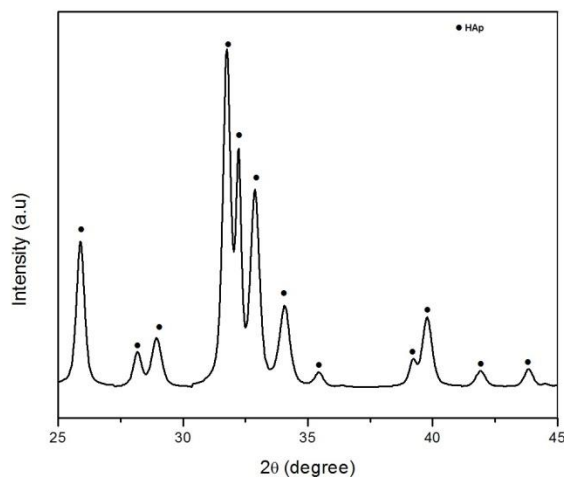
## **2. Materials and methods**

### **2.1. Materials**

Hydroxyapatite  $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$  samples were prepared using calcium nitrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), diammonium hydrogen phosphate  $((\text{NH}_4)_2\text{HPO}_4)$ , and ammonia, which were purchased from Merck. Commercial  $\text{TiH}_2$  (325 mesh powder) was procured from Alfa Aesar.

### **2.2. Powder synthesis**

The HAp powder was prepared by wet chemical precipitation method. Stoichiometric amount of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  was gradually added into solution of  $(\text{NH}_4)_2\text{HPO}_4$ , with stirring. Ammonia was added drop wise into the mixed solution with vigorous stirring until pH reached a value of around 10 to 11, and was continued for 2 -3 hours to allow the reaction to take place towards completion. A white precipitate was obtained and was aged for 12 hours at room temperature. The obtained precipitate was filtered, washed with deionized water for 3-4 times and dried at  $110^\circ\text{C}$  for 24 hours. The dried lumps were crushed using an agate mortar and calcined at  $700^\circ\text{C}$ . The powder was confirmed as pure hydroxyapatite by matching the XRD pattern obtained (**Fig.1**) using D8 Advance (Bruker) analytical x-ray system with JCPDS file 09-0432.



**Fig.1.** XRD pattern of pure HAp calcined at  $700^\circ\text{C}$

### 2.3. Pellet Formation

$\text{TiH}_2$  was added in different weight percentages of 5, 10, 15 and 20 to HAp, and mixed with pestle and mortar for homogenous mixing. Pellets of 10mm diameter were prepared using

uniaxial press under 150 bars load. The as-mixed composite powders and pellets of HAp/TiH<sub>2</sub> were dried at 110°C for 24 hours and firing was done in a muffle furnace at temperatures of 900°C, 1000°C, 1100°C and 1200°C with 3°C per minute heating rate and 2 hours soaking at the maximum temperature.

## 2.4. Sample characterization

Phase analysis and lattice parameters of sintered HAp/TiH<sub>2</sub> powders were determined by X-ray diffraction (XRD) using Bruker D8 advance analytical x-ray system. The XRD patterns of the samples were obtained by using OriginPro software. An estimation of the crystallite size was obtained using the Debye-Scherrer equation (1)

$$D = \frac{K\lambda}{\beta \cos\theta} \dots\dots\dots(1)$$

where,

$\beta$  is the peak width at half maximum intensity(FWHM) (in radians)

K is the Scherrer constant dependent on crystal habit (0.9)

$\lambda$  is the wavelength of X-rays (1.5406Å for CuK <sub>$\alpha$</sub>  radiation)

D is the crystallite size (nm)

$\theta$  is Bragg's diffraction angle(°)

The lattice constants of the HAp/TiH<sub>2</sub> powders were determined by the following relation(2)

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + k^2 + l^2}{a^2} \right) + \frac{l^2}{c^2} \dots\dots\dots(2)$$



The volume of the hexagonal unit cell of the materials was calculated according to the formula,  
 $V=0.866a^2c$ ..... (3)

where, V is the volume of unit cell (nm<sup>3</sup>), a and c are the lattice constants.

Scanning electron microscopic (SEM) analysis (Quanta 200 FEG) was used for analyzing the size and morphology of sintered HAp/TiH<sub>2</sub> powders. FTIR (PerkinElmer) was performed to assess the functional groups and chemical composition of the sintered HAp/TiH<sub>2</sub> powders, for which the powders were mixed with KBr and pelletized, and spectra was obtained between 4000 – 400 cm<sup>-1</sup>.

The density and porosity of the sintered HAp/TiH<sub>2</sub> pellets were tested by Archimede's principle with water as fluid and calculated using the formula (4) and (5) respectively

Apparent porosity (%) is  $\frac{S-D}{S-I} \times 100$  .....(4)

Apparent (bulk) density (g/cc) is  $\frac{D}{S-I}$  .....(5)

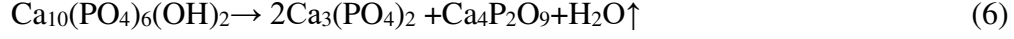
where, S is weight of the soaked piece (gm), D is weight of the dry piece (gm), I is weight of the immersed piece (gm).

### **3. Results and discussion**

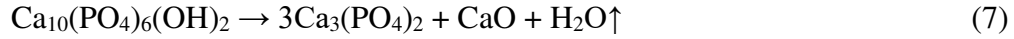
#### **3.1.Structural characterization**

The decomposition characteristics of HAp are reported variedly in literatures. It was reported that at sintering temperatures from 650°C to 1200°C, HAp decomposes into β-tricalcium phosphate [25]. The decomposition of HAp to Tri Calcium Phosphate (TCP –

$\text{Ca}_3(\text{PO}_4)_2$ ) and Tetra Calcium phosphate (TTCP –  $\text{Ca}_4(\text{PO}_4)_2\text{O}$ ) occur at temperatures greater than  $1200^\circ\text{C}$  according to the reaction given in eq.(6) [26].



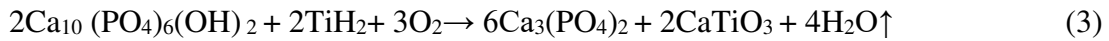
The following formula was proposed to account for the decomposition of HAp when it is sintered to higher temperature ( $1350^\circ\text{C}$ ) [27].



According to equations (6) and (7), both the decomposition and dehydroxylation reactions include water vapour as a by-product, and the rates at which these reactions continue depend on the moisture in the furnace atmosphere. Thus, the secondary phase formation during sintering could be controlled by controlling the sintering atmosphere. High amount of humidity present in sintering atmosphere has the tendency to delay decomposition rate by inhibiting the dehydration of  $\text{OH}^-$  group from the HAp matrix. This can be attained by controlling the partial pressure of the atmosphere, as the saturated moisture content in the atmosphere would suppress the by-product of water vapour between the reactions of both the dehydroxylation and decomposition [28]. In general, sintering at elevated temperatures tends to take the  $\text{OH}^-$  (hydroxide group) in the HAp matrix and concludes in the decomposition of HAp into  $\alpha$ -TCP,  $\beta$ -TCP and TTCP [25, 29].

Fig.2 gives the X-ray spectra of the HAp/ $\text{TiH}_2$  sintered at different temperatures, and it reveals the presence of HAp, decomposition phases of HAp and a new phase relative to  $\text{CaTiO}_3$  traces which indicates the interaction between HAp and  $\text{TiH}_2$ . According to the phase compositions, it is obvious that  $\text{CaTiO}_3$  is a product of reaction between  $\text{TiO}_2$  and  $\text{CaO}$ , which is one of the decomposition products of HAp (according to Eq. (7)).  $\text{CaTiO}_3$  was registered in the

XRD pattern of composite powders (irrespective of TiH<sub>2</sub> content) in Fig. 2, but there was no evidence of TiO<sub>2</sub>, suggesting high thermodynamic tendency of TiH<sub>2</sub> to diffuse and then to react with HAp. However, the formation of CaTiO<sub>3</sub> indicates that the reaction between HAp and TiH<sub>2</sub> has taken place during thermal treatment. Hence, the interaction between TiH<sub>2</sub> and HAp at higher temperature (>900°C) is proposed as in equation (3).

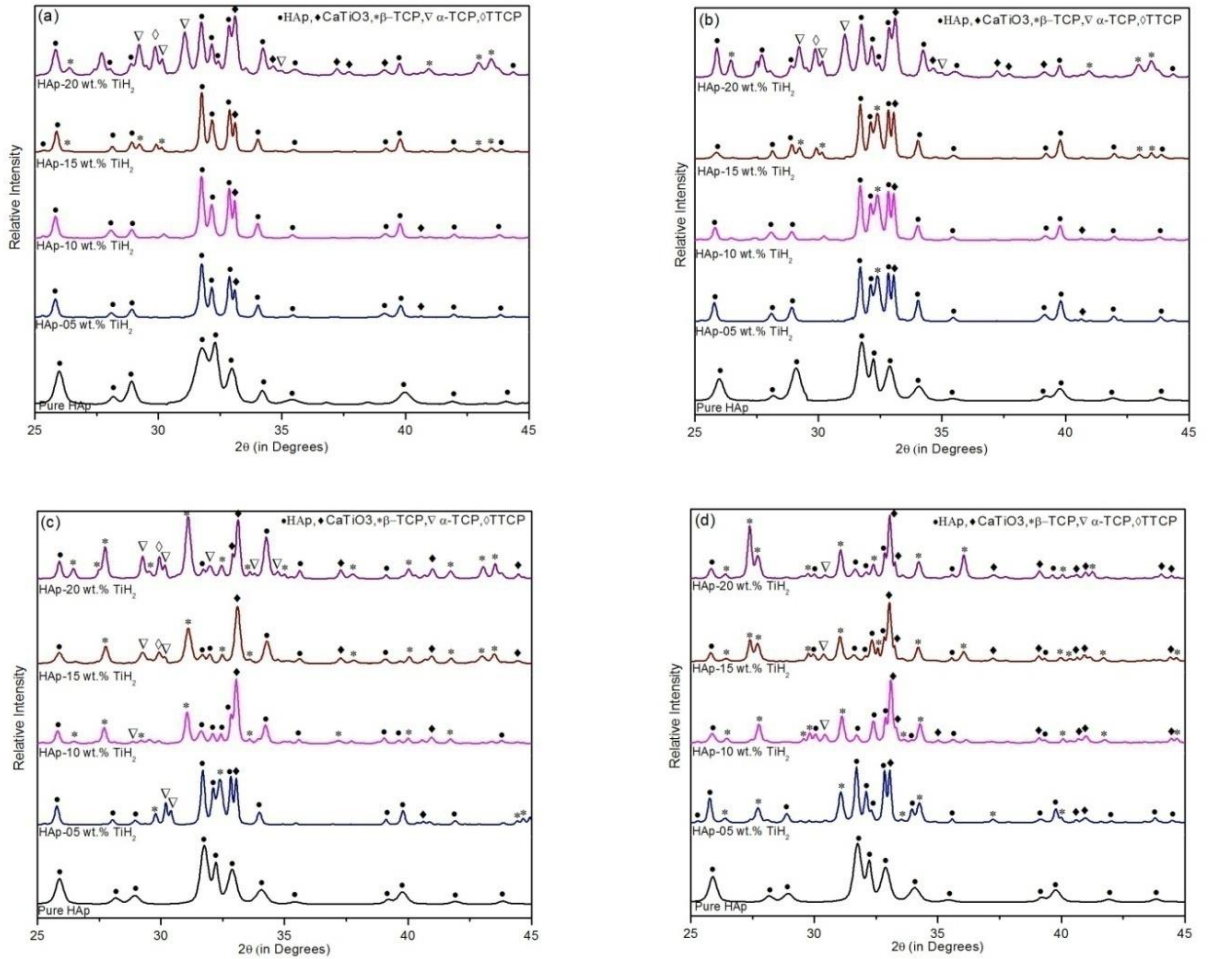


Diffraction peaks from CaTiO<sub>3</sub> were observed from 900°C onwards, and its intensity was found to increase with increasing percentage of TiH<sub>2</sub> while that of apatite peaks decreased. The sharpness of CaTiO<sub>3</sub> peaks increased with the sintering temperature hinting on the increased crystallinity. The HAp decomposition phase formed at a particular temperature was found to be influenced by the TiH<sub>2</sub> content and the traces of pure HAp was found to remain undecomposed till 1200°C. The HAp decomposition phases were observed from 15wt% TiH<sub>2</sub> at 900°C, and 5wt% TiH<sub>2</sub> at 1000°C and the major phase was found to be β-TCP. Traces of α-TCP and TTCP formation at 900°C and 1000°C was found only on addition of 20wt% TiH<sub>2</sub>.

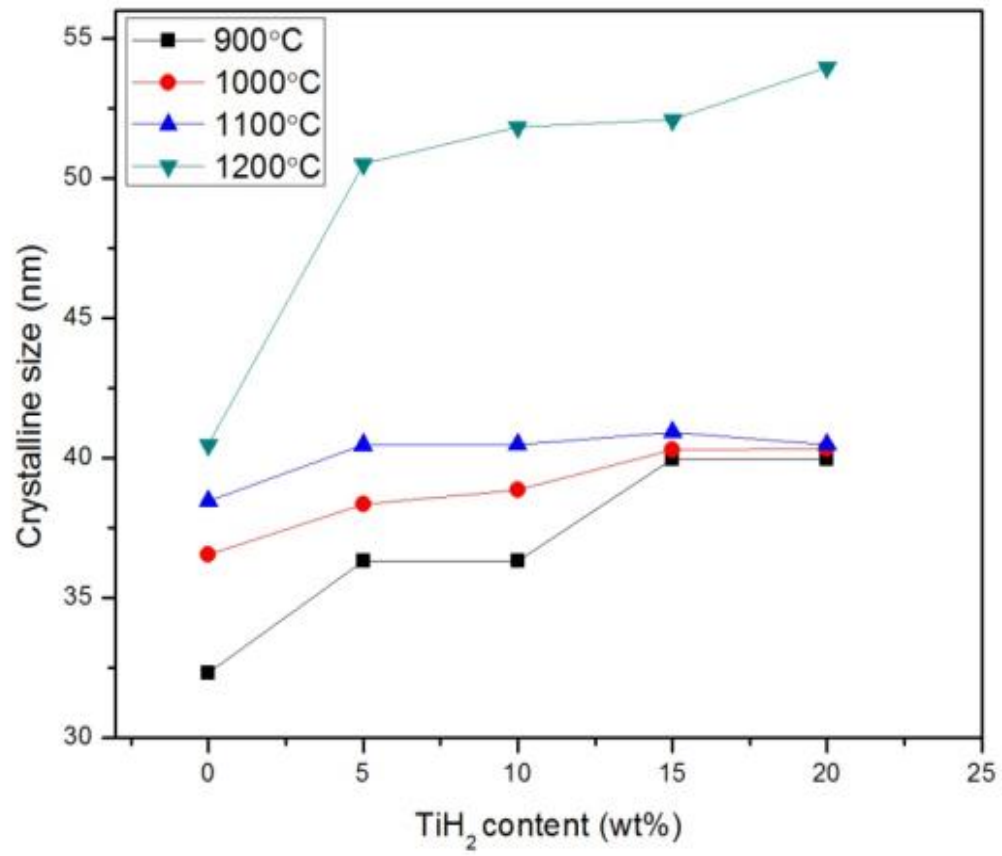
Contrary to the above observations, α-TCP formation had initiated from 5wt% TiH<sub>2</sub> at 1100°C but the peaks became prominent only above 15wt% TiH<sub>2</sub>. The other decomposition phase obtained with α-TCP was β-TCP. TTCP formation was observed from 15wt% TiH<sub>2</sub> at 1100°C. Samples sintered at 1200°C were observed to have CaTiO<sub>3</sub> and β-TCP as their major phases at various TiH<sub>2</sub> content. Additionally, minor peaks of α-TCP were found from 10wt% TiH<sub>2</sub>. TTCP peaks was absent at 1200°C.

Fig.3, presents the crystallite size versus TiH<sub>2</sub> content at different sintering temperature ranging from 900 to 1200°C. The crystallite size was found to increase with increasing amount

of  $\text{TiH}_2$ , and with increase in sintering temperature. The increase in the crystallite size with increase in the sintering temperature can be attributed to crystal growth and densification. The lattice constants of HAp/ $\text{TiH}_2$  was evaluated for all the sintered HAp/ $\text{TiH}_2$  samples and are listed in Table 1 & 2. These values were found not to vary appreciably as a function of  $\text{TiH}_2$  content and heat treatment temperature.



**Fig.2.** XRD peaks obtained after sintering at temperatures of (a) 900°C (b) 1000°C (c) 1100°C and (d) 1200°C for HAp with different  $\text{TiH}_2$  contents



**Fig.3.** Plot of the crystallite size vs. TiH<sub>2</sub> content at various temperatures

**Table 1.**

Crystallite size, Lattice parameter and Cell volume of HAp with different TiH<sub>2</sub> content at 900°C and 1000°C

Temperature →		900°C			1000°C			
Sample Name↓	Ds	a(Å)	c(Å)	V(Å <sup>3</sup> )	Ds (nm)	a(Å)	c(Å)	V(Å <sup>3</sup> )
	(nm)							
HAp-05wt.% TiH <sub>2</sub>	36.3391	9.426	6.889	530.1	38.5390	9.428	6.889	530.2
HAp-10wt.% TiH <sub>2</sub>	36.3395	9.422	6.879	528.9	38.6127	9.425	6.878	529.1
HAp-15wt.% TiH <sub>2</sub>	39.9770	9.425	6.888	529.9	39.9956	9.423	6.892	529.9
HAp-20wt.% TiH <sub>2</sub>	39.9743	9.443	6.877	531.0	39.9923	9.433	6.890	530.9

**Table 2.**

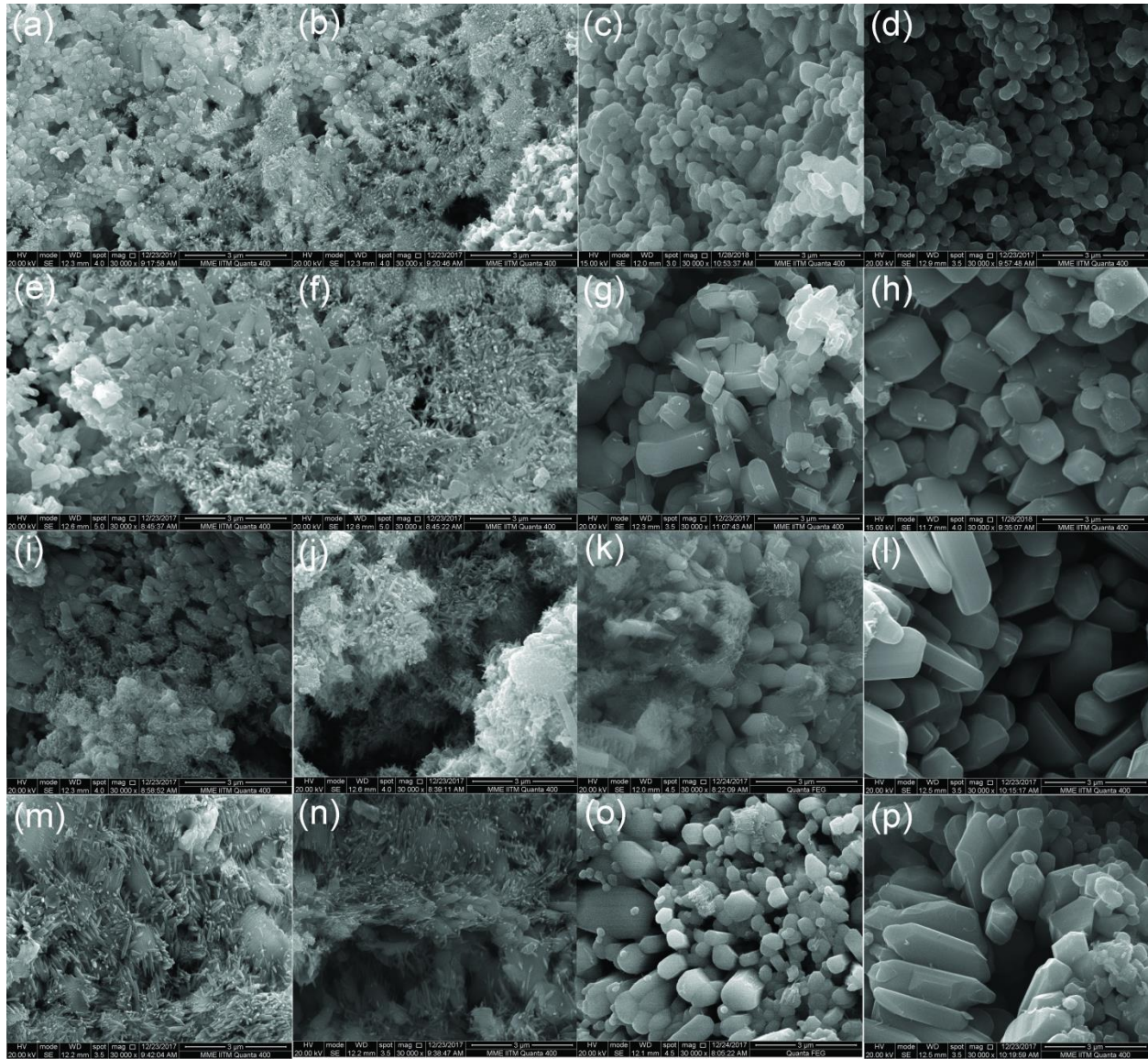
Crystallite size, Lattice parameter and Cell volume of HAp with different TiH<sub>2</sub> content at 1100°C and 1200°C

Temperature →		1100°C			1200°C			
Sample Name↓	Ds	a(Å)	c(Å)	V(Å <sup>3</sup> )	Ds (nm)	a(Å)	c(Å)	V(Å <sup>3</sup> )
	(nm)							
HAp-05wt.% TiH <sub>2</sub>	40.4836	9.419	6.880	528.6	50.5138	9.429	6.888	530.4
HAp-10wt.% TiH <sub>2</sub>	40.4860	9.419	6.881	528.7	51.8497	9.429	6.877	529.5
HAp-15wt.% TiH <sub>2</sub>	40.9410	9.438	6.879	530.8	52.0920	9.423	6.893	530.0
HAp-20wt.% TiH <sub>2</sub>	40.4917	9.426	6.880	529.4	53.9825	9.419	6.879	528.6

### 3.2.Morphological Characterization

Small diameter elongated particles having needle like appearance, were observed on samples sintered at 900°C & 1000°C irrespective the amount of TiH<sub>2</sub> added. These particles can be confirmed to be CaTiO<sub>3</sub> from the XRD patterns (Fig. 2. a & b) for a particular percentage of TiH<sub>2</sub> added, the distribution of CaTiO<sub>3</sub> particles was more at 1000°C when compared to that at 900°C. As the sintering temperature increased to 1100°C and 1200°C, these smaller particles became coarser and elongated due to enhanced crystal growth of CaTiO<sub>3</sub> which can be confirmed with the sharpening of XRD peaks as observed from Fig. 2.c&d. Average grain size was increased upto 1.468µm and 1.890µm at the corresponding sintering temperature of 1100°C and 1200°C.





**Fig.4.** SEM micrographs showing different morphological characteristics: (a), (e), (i) and (m) HAp-5%,10%,15% and 20% TiH<sub>2</sub> sintered at 900°C; (b) (f), (j) and (n) HAp-5%,10%,15% and 20% TiH<sub>2</sub> sintered at 1000°C; (c) (g), (k) and (o) HAp-5%,10%,15% and 20% TiH<sub>2</sub> sintered at 1100°C, (d) (h), (l) and (p) HAp-5%,10%,15% and 20% TiH<sub>2</sub> sintered at 1200°C.

### 3.3. FTIR Analysis

The FTIR spectrum of the samples heat treated at 900°C, 1000°C, 1100°C and 1200°C without and with different percentages of TiH<sub>2</sub> are shown in Fig.5. Most bands characterize the phosphate group of HAp, especially at 570 cm<sup>-1</sup>, 605 cm<sup>-1</sup>, 1038-1049 cm<sup>-1</sup> and 1119 - 1120cm<sup>-1</sup> as mentioned in Table.3. A sharp peak with weak intensity corresponding to OH<sup>-</sup> stretching vibration band is observed at 3571 cm<sup>-1</sup> in pure HAp sample. This band is totally absent at higher TiH<sub>2</sub> content or at higher temperature due to the dehydroxylation as a result of HAp decomposition . Weak bonds at 944cm<sup>-1</sup> and 550 cm<sup>-1</sup> related to the secondary β-TCP phase in HAp were observed in all HAp/TiH<sub>2</sub> samples. The peak at 605 cm<sup>-1</sup> are assigned to the asymmetric deformation of the PO<sub>4</sub><sup>3-</sup> ions (ν<sub>1</sub>). The peaks at 944 cm<sup>-1</sup>and 962 cm<sup>-1</sup> are relative to the symmetric stretching of the PO<sub>4</sub><sup>3-</sup> ions (ν<sub>3</sub>) and the peaks at 1038 – 1090 cm<sup>-1</sup> and 1119 - 1120 cm<sup>-1</sup> are relative to the asymmetric stretching of the PO<sub>4</sub><sup>3-</sup> ions (ν<sub>3</sub>). Furthermore, the relative intensity between the peaks at ~478 cm<sup>-1</sup> and that at ~470 cm<sup>-1</sup> reflects the degree of the dehydroxylation. The peak at 478 cm<sup>-1</sup> is slightly stronger than the peak at 470 cm<sup>-1</sup>. In addition to the above mentioned peaks, few other peaks are also detected at around 2350 and 2923 cm<sup>-1</sup> which are due to KBr used for sample preparation [30].

**Table 3.**

Observed FTIR band positions and their assignment.

Sample Name →	Pure HAp	HAp-05wt.% TiH <sub>2</sub>	HAp-10wt.% TiH <sub>2</sub>	HAp-15wt.% TiH <sub>2</sub>	HAp-20wt.% TiH <sub>2</sub>	Assignment	References
Temperature ↓	Vibrational frequency (cm <sup>-1</sup> )						
	470.59	-	-	-	-	ν <sub>2</sub> bending mode of P-	[31]

						O mode	
900°C	570.95	570.95	570.95	570.95	570.95	O-P-O bending	[32]
	601.74	601.84	601.84	601.84	601.84	$\nu_4$ bending mode of O-P-O mode	[31,32]
	632.60	632.67	632.67	632.67	632.67	$\nu_4$ ( $\text{PO}_4^{3-}$ )	[34]
	-	962.52	962.52	962.52	962.52	$\nu_3$ ( $\text{PO}_4^{3-}$ )	[31]
	1049.19	1043.53	1043.53	1043.53	1043.53	$\nu_3$ ( $\text{PO}_4^{3-}$ )	[34]
	2360.69	2360.97	2360.97	2360.97	2381.22	-	[30]
	3571.90	3571.36	3571.36	3571.36	3571.36	The vibrational of OH <sup>-</sup>	[34,35]
1000°C	~478.31	-	-	-	-	Dehydroxylation	[35]
	570.88	567.09	567.09	567.09	567.09	$\nu_4$ ( $\text{PO}_4^{3-}$ )	[34]
	606.6	606.6	606.6	606.6	606.6	$\nu_4$ ( $\text{PO}_4^{3-}$ )	[34]
	-	944.20	944.20	944.20	944.20	$\nu_2$ ( $\text{PO}_4^{3-}$ )	[33]
	1049.19	1041.61	1041.61	1041.61	1041.61	$\nu_3$ ( $\text{PO}_4^{3-}$ )	[34]
	-	1120.69	1120.69	1120.69	1120.69	$\nu_3$ ( $\text{PO}_4^{3-}$ )	[33]
	2360.69	2363.86	2363.86	2363.86	2363.86	-	[30]
1100°C	478.31	-	-	-	-	Dehydroxylation	[35]
	570.88	550.70	550.70	550.70	550.70	$\nu_4$ ( $\text{PO}_4^{3-}$ )	[34]
	605.67	605.67	605.67	605.67	605.67	$\nu_1$ ( $\text{PO}_4^{3-}$ )	[33]
	-	944.19	944.19	944.19	944.19	$\nu_2$ ( $\text{PO}_4^{3-}$ )	[33]
	1049.19	1041.60	1041.60	1041.60	1041.60	$\nu_3$ ( $\text{PO}_4^{3-}$ )	[34]
	-	1119.72	1119.72	1119.72	1119.72	$\nu_3$ ( $\text{PO}_4^{3-}$ )	[33]
	2360.69	2360	2360	2360	2360	-	[30]
1200°C	478.31	-	-	-	-	Dehydroxylation	[35]
	563.17	550.70	550.70	550.70	550.70	$\nu_4$ ( $\text{PO}_4^{3-}$ )	[34]
	-	604.70	603.74	603.74	602.78	$\nu_1$ ( $\text{PO}_4^{3-}$ )	[33]
	-	944.19	944.19	944.19	944.19	$\nu_2$ ( $\text{PO}_4^{3-}$ )	[33]
	1049.19	1042.56	1042.56	1042.56	1042.56	$\nu_3$ ( $\text{PO}_4^{3-}$ )	[34]
	2360.69	2360	2360	2360	2360	-	[30]

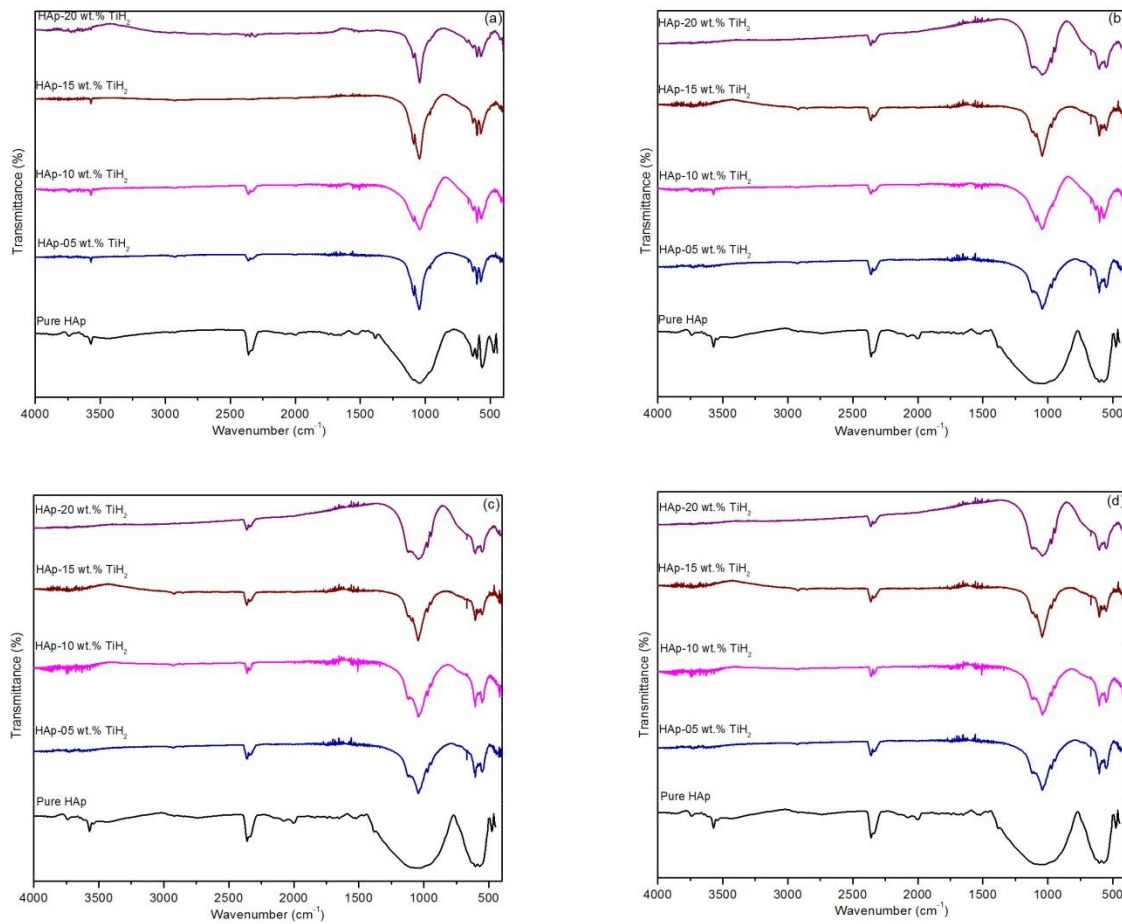
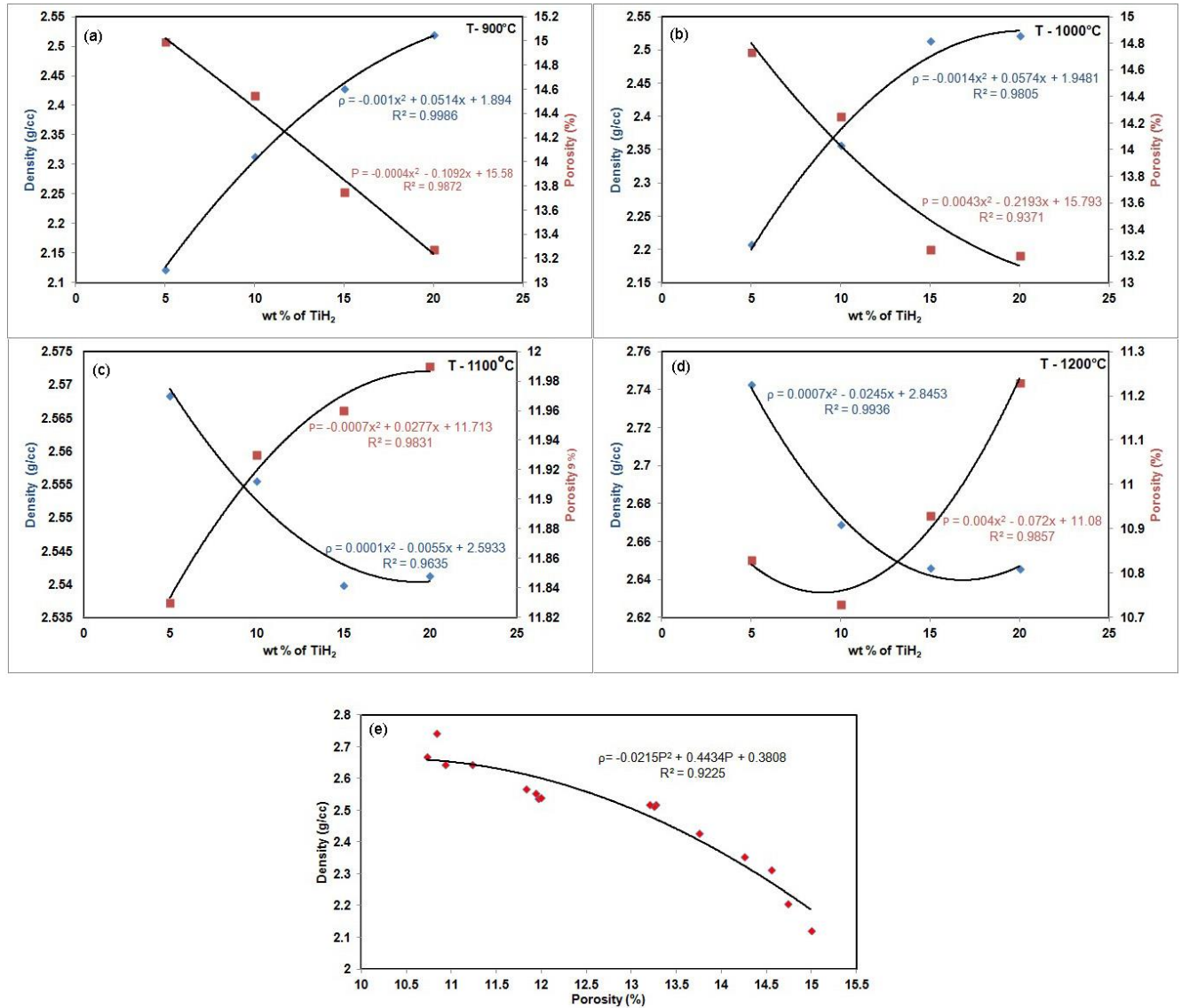


Fig.5.FT-IR spectra obtained after sintering at (a) 900°C, (b) 1000°C, (c) 1100°C and (d) 1200°C from various HAp-TiH<sub>2</sub> composites

### 3.4. Density and Porosity

Density of HAp/TiH<sub>2</sub> composite was found to increase with increase in TiH<sub>2</sub> weight percentage at 900°C and 1000°C. Density values decreased above 1000°C due to the decomposition of HAp, due to which the porosity of the composite has increased. As can be observed from the SEM images (Fig. 4) of HAp/TiH<sub>2</sub> samples heat treated at 900°C and 1000°C, formation of CaTiO<sub>3</sub> needle structures have filled the void spaces resulting in increased density. Above 1000°C, CaTiO<sub>3</sub> crystals were observed to grow proportionately with increasing

TiH<sub>2</sub> content and temperature. This leads to more open structure leading to decrease in density with increase in TiH<sub>2</sub> content at 1100°C and 1200°C. Corresponding inverse correlation for porosity was observed in all samples.



**Fig.6.** Density and porosity graph of HAp with different weight percentages of TiH<sub>2</sub> (a) sintered at 900°C (b) sintered at 1000°C (c) sintered at 1100°C(d) sintered at 1200°C(e) Overall graph of density vs porosity.



Fig.6.e. shows the overall graph for the density and porosity values, and shows that increase in density decreases the porosity of sample. The correlation co-efficient calculated from the graph drawn between the overall density and porosity was 0.9225.

## Conclusions

Hydroxyapatite was prepared by precipitation method and powders of hydroxyapatite with different  $\text{TiH}_2$  percentage were sintered in air atmosphere at the range of 900-1200°C for 2 h for simultaneously developing pore in the HAp and incorporate it with Titania. The experimental result from XRD clearly reveals that the product composition leads to TCP and  $\text{CaTiO}_3$  major phases. SEM results showed that grain size increased at 1200°C with increase in wt % of  $\text{TiH}_2$ . The outcome of the sintering studies carried out shows that the maximum porosity was obtained at 5wt% of  $\text{TiH}_2$  addition to HAp at sintering temperatures of 900°C and 1000°C. The incidence of broad sintering reactions and phase dissociation of HAp leads to development of TCP– $\text{CaTiO}_3$  composites. The mechanical properties and bioactivity of the samples will be studied in future.

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Figures

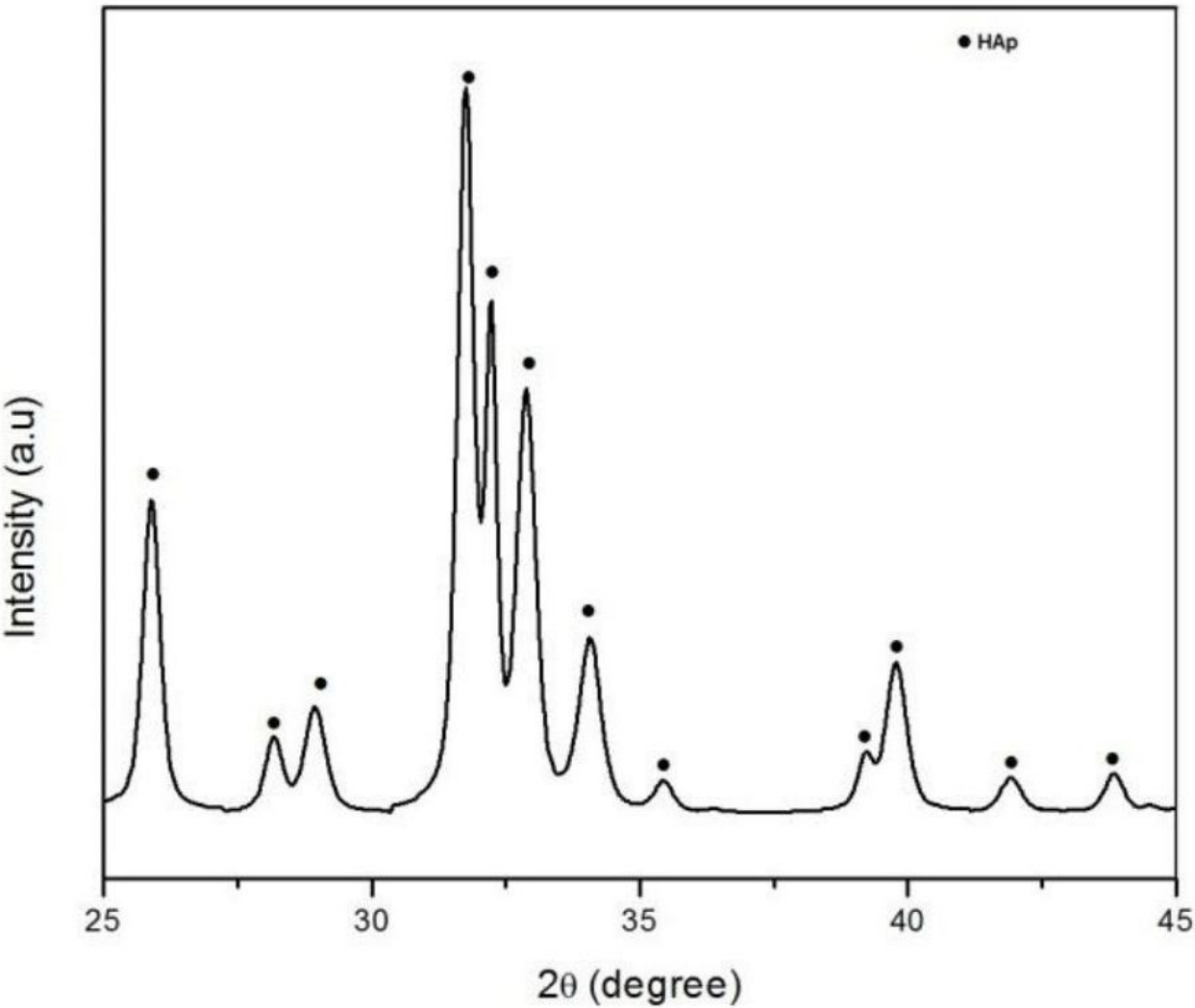
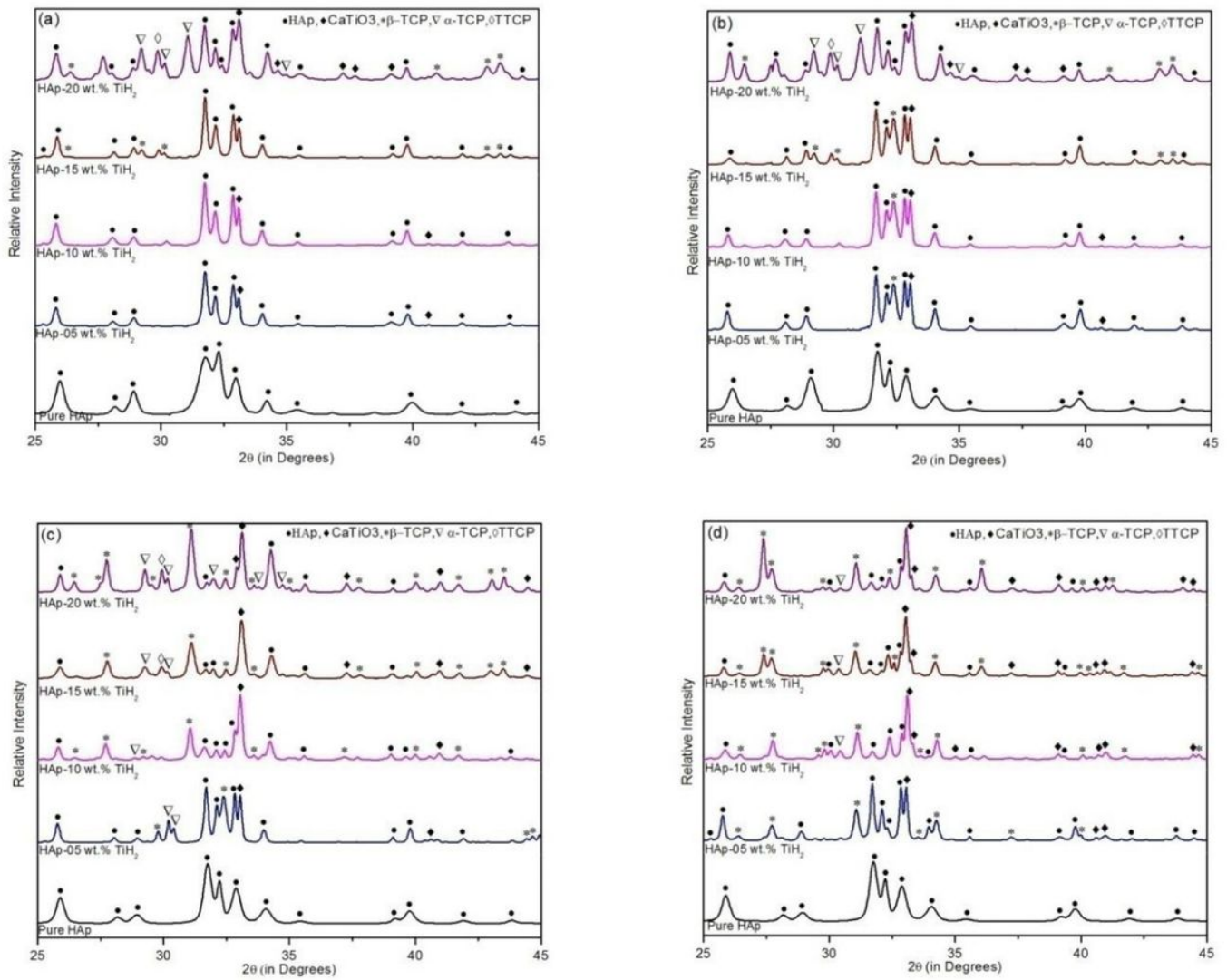


Figure 1

XRD pattern of pure HAp calcined at 700°C



**Figure 2**

XRD peaks obtained after sintering at temperatures of (a) 900°C (b) 1000°C (c) 1100°C and (d) 1200°C for HAp with different  $\text{TiH}_2$  contents

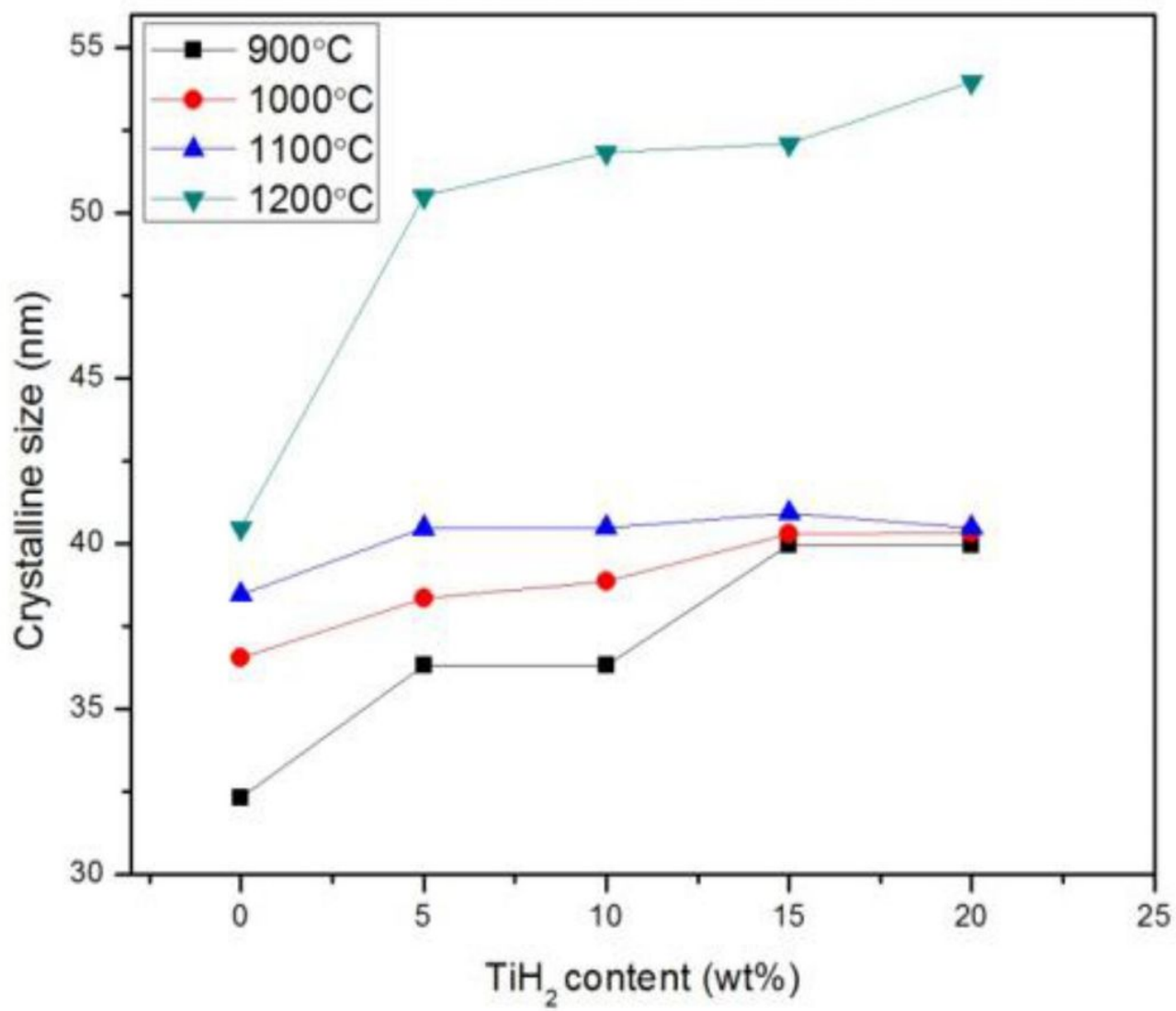
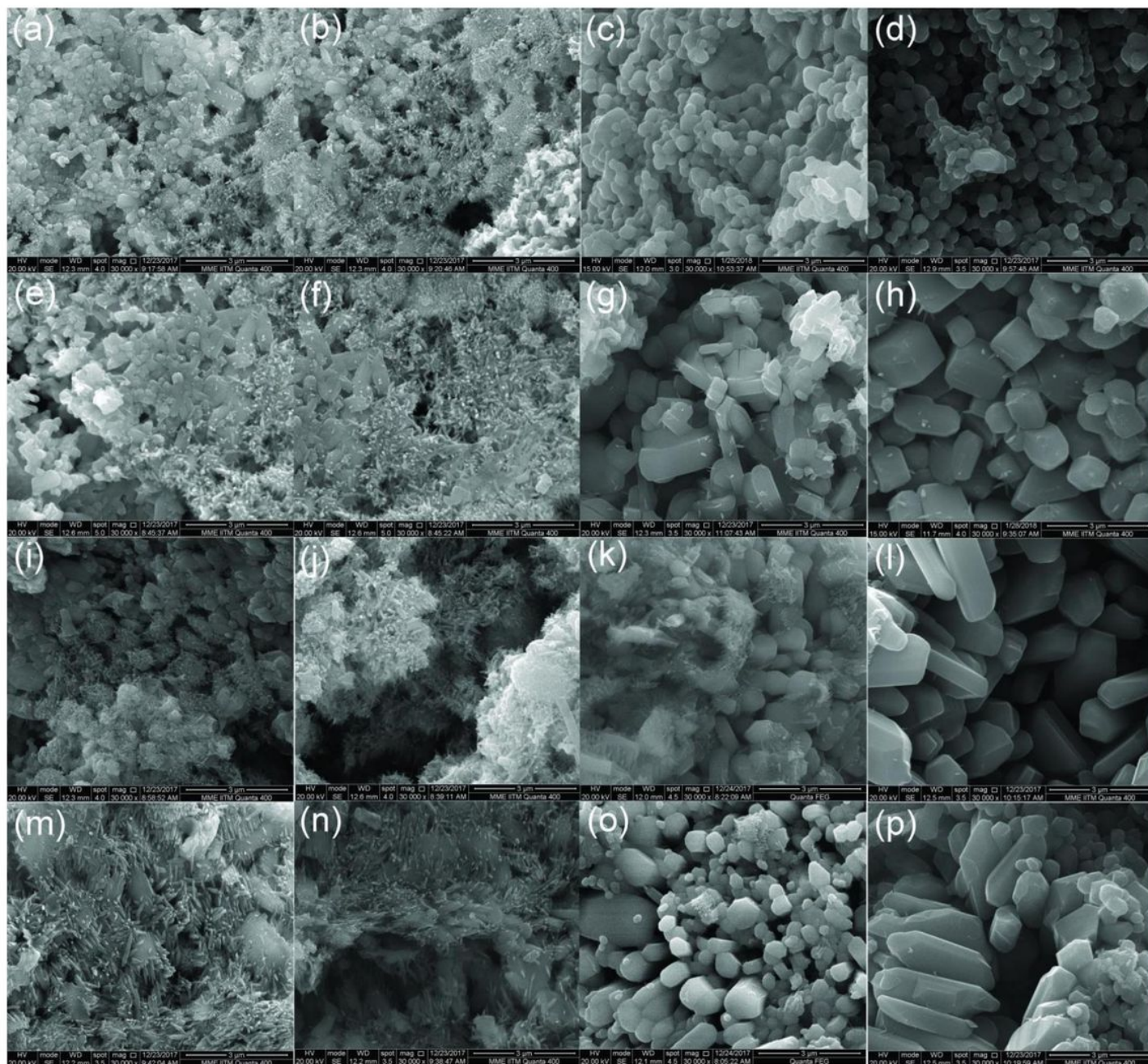


Figure 3

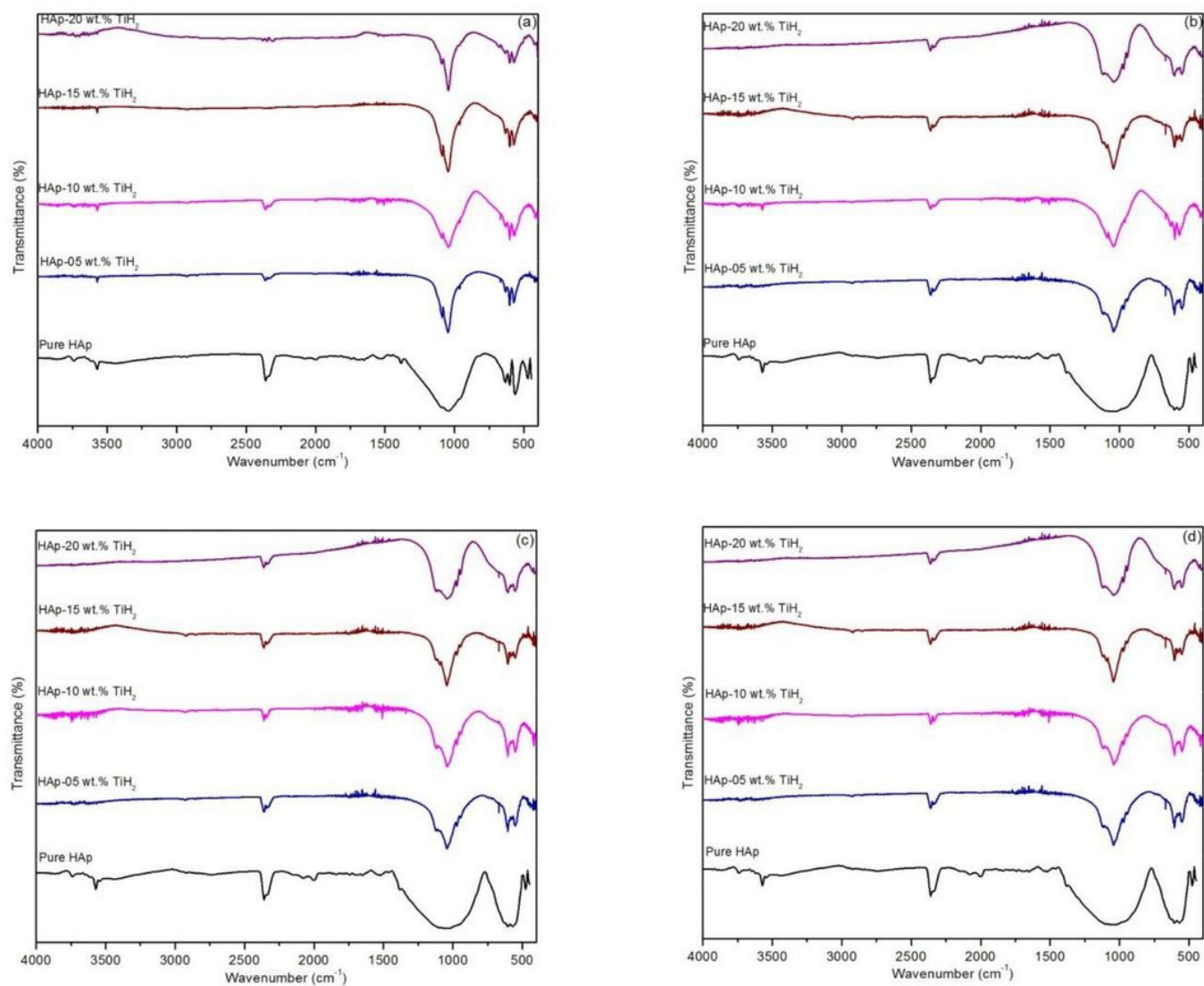
Plot of the crystallite size vs. TiH<sub>2</sub> content at various temperatures



**Figure 4**

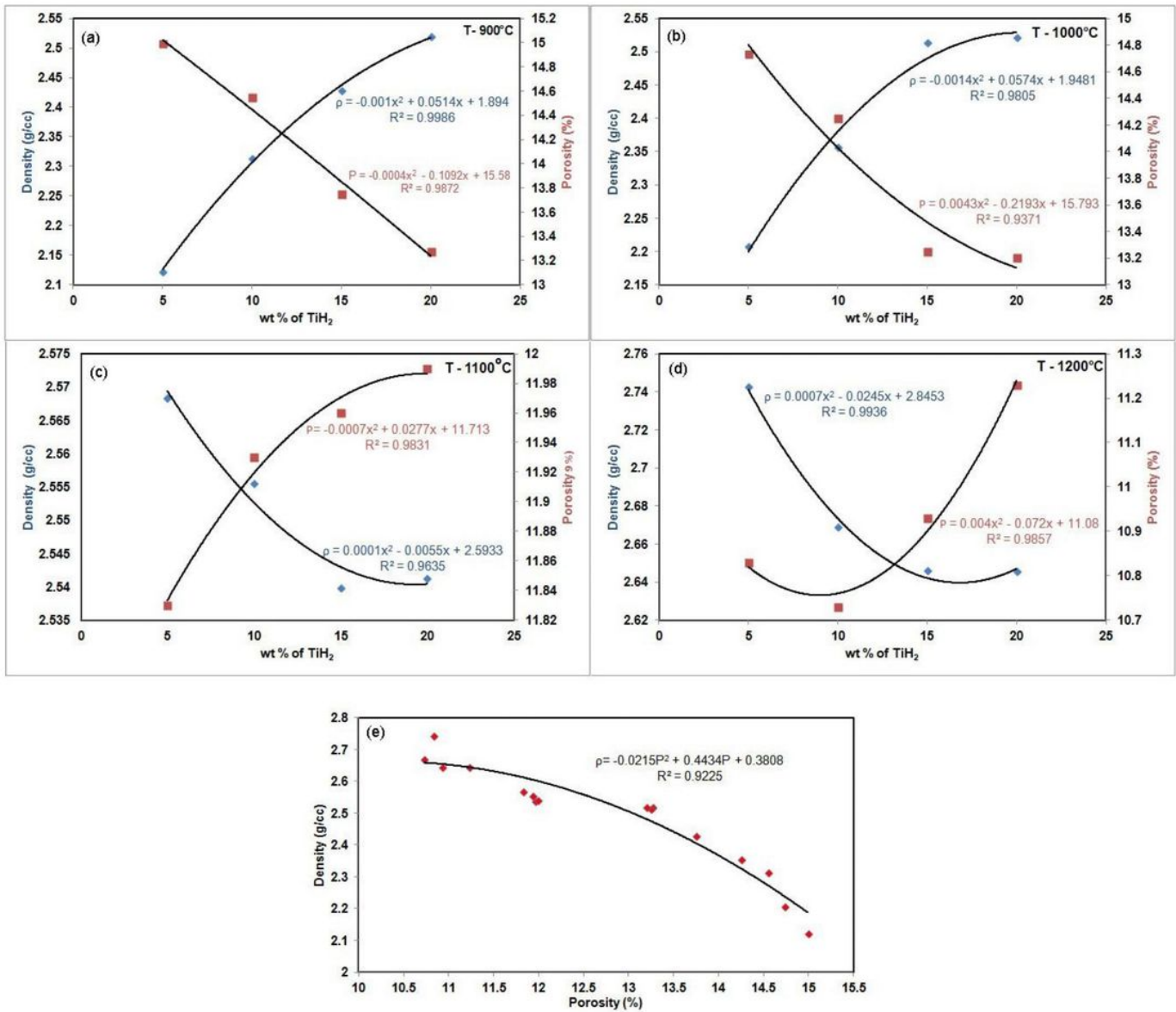
SEM micrographs showing different morphological characteristics: (a), (e), (i) and (m) HAp-5%,10%,15% and 20% TiH<sub>2</sub> sintered at 900°C; (b) (f), (j) and (n) HAp-5%,10%,15% and 20% TiH<sub>2</sub> sintered at 1000°C; (c) (g), (k) and (o) HAp-5%,10%,15% and 20% TiH<sub>2</sub> sintered at 1100°C, (d) (h), (l) and (p) HAp-5%,10%,15% and 20% TiH<sub>2</sub> sintered at 1200°C.





**Figure 5**

FT-IR spectra obtained after sintering at (a) 900°C, (b) 1000°C, (c) 1100°C and (d) 1200°C from various HAp-TiH<sub>2</sub> composites



**Figure 6**

Density and porosity graph of HAp with different weight percentages of  $\text{TiH}_2$  (a) sintered at 900°C (b) sintered at 1000°C (c) sintered at 1100°C (d) sintered at 1200°C (e) Overall graph of density vs porosity.