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Controlled growth and investigations on the morphology and mechanical properties of hydroxyapatite/titania nanocomposite thin films

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ABSTRACT

In this paper, the focus is on understanding the properties of nanocomposite hydroxyapatite (HAp)/titania (TiO_2) thin films with respect to TiO_2 concentration. HAp/TiO_2 nanostructured composite thin films with different TiO_2 concentrations were successfully fabricated by a simple sol–gel dip coating method. Highly stable HAp and TiO_2 sols were prepared prior to the formation of nanocomposite thin films. The coatings were performed under controlled dipping and heat treatment processes. Phase pure HAp and TiO_2 were well developed in the nanocomposite after the heat treatment and this was confirmed by XRD. The SEM and AFM analyses of HAp/TiO_2 nanocomposite coatings show the variation in the morphology as a consequence different TiO_2 concentration. This shows a reduction in the particle size to nanoscale due to the addition of TiO_2. The mechanical strength of the coating also increased upon the addition of TiO_2 as determined by nanoindentation. The composite thin films with 50 and 80 vol.% of TiO_2 show good mechanical strength when compared to other concentrations of TiO_2.

1. Introduction

The preparation and application of nanostructured thin films with specific size and morphology has motivated much research interest because of their novel morphology dependent physical properties and immense applications in technologically important areas. The biomedical use of synthetic materials (biomaterials) has found remarkable revolution and now it is one of the best research areas in material science. Various metals, ceramics and polymers have been investigated over several decades for orthopedic and dental applications. Among the various materials, hydroxyapatite (HAp) and titanium compounds (metallic, oxides or nitrides) are found to be the most suitable biomaterials. The major inorganic constituent of bones and teeth is calcium phosphate, whose composition is similar to that of synthetic hydroxyapatite (HAp; $Ca_{10}(PO_4)_6OH)_2$. This similarity provides HAp based materials excellent bioactivities like bone bonding capability, osteoconductivity, and biocompatibility [1].

Successful bone fixation has been shown to be related to the surface morphology and composition of the material. Hence along with composition, the morphological characteristics of HAp particles such as shape, size and uniform size distribution which mimesis the bone nanostructures play a vital role in the mechanical, chemical and biological activities [2].

The major disadvantage of HAp is its poor adhesion, poor mechanical integrity, high brittleness, degradation in acidic/basic conditions and incomplete bone growth which restricts its application only in non load-bearing areas of the human body. In general, the creation of nanostructures of ceramic materials with grain/particle size less than $\sim$100 nm can significantly improve the bioactivity of the implant and enhance the osteoblast adhesion [3,4]. Motivated by that, an attempt has been made to introduce titanium compounds to HAp for improving its properties. The addition of biocompatible TiO_2 to HAp is expected to give better strength and corrosion resistance in extreme conditions. Also, HAp in nanometer size deposits in an orderly way on the cologne matrix in natural bone [5]. However, a good understanding of the composite coating formation mechanism and structure characterization is necessary to contribute considerably for the development of the reinforced bioceramic coatings [3]. Hence the formation and understanding of the formation mechanism of hydroxyapatite and its composite thin films has attracted much attention in recent times, since such coatings improve the biocompatibility, bioactivity and also the mechanical strength of the implants.

The present work aims at preparing a composite thin film comprising HAp on TiO_2 matrix by sol–gel process and study how the different concentration of titania influences on the microstructural

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and mechanical properties. Since many reports are lacking with the morphological changes and their corresponding properties for the bioactive coatings, this study is mainly focusing on the nanostructural morphological variations with respect to the TiO_2 concentration. Also many reports are available about the HAp coating on the metal and Ti alloys. Thus, we want to prepare the HAp/TiO_2 composite for optically plane surfaces which can be further extended to improve the mechanical and adhesion property of bioactive glasses, borosilicate glasses which is also used for biomedical applications. Hence we choose the optically plain glass substrate for coating the composite films. In our previous report, the nanoparticles of HAp/titania nanocomposites were prepared and studied the influence of titania on the microstructural and mechanical behavior [6]. There we observed that the titania enhances the microstructual and mechanical behavior. Hence we wanted to extend the work to make the thin films of the HAp/TiO_2 on optically plain surface and study their morphological and mechanical behavior. Hence the present study mainly concentrates on improving the surface morphology and simultaneously enhances the mechanical strength using TiO_2 addition.

2. Materials and methods

2.1. Preparation of HAp/TiO_2 nanostructured composite coatings

Hydroxyapatite sol was prepared by using calcium nitrate [$Ca(NO_3)_2 \cdot 4H_2O$] and phosphoric acid [H_3PO_4] as calcium and phosphorus precursors respectively. Stoichiometric HAp was prepared by dissolving 1.67 M calcium nitrate in 2-methoxy ethanol and it was stirred for 30 min. 1 M Phosphoric acid was added drop wise to calcium containing solution under vigorous stirring, to maintain the Ca/P ratio as 1.67. After one hour of stirring a transparent solution was obtained, and this was kept for 24 h with mild stirring to increase the viscosity of the sol to prepare thin films.

Titanium tetra isopropoxide (TTIP) was used as a titanium precursor. The titanium alkoxide used in this study is highly unstable in air. So, the chelated TiO_2 sol was prepared by using acetyl acetone as a ligand and HCl as acid catalyst. Initially 1 M TTIP was mixed with 2-methoxy ethanol. The 0.5 M acetyl acetone and 0.25 M HCl was added drop wise to the above solution under vigorous stirring. Finally, the required amount of water was added slowly under stirring condition. After vigorous stirring for 30 min the obtained transparent solution was kept for 24 h with mild stirring, for further use in film preparation. Both the experiments were carried out at room temperature.

Optically plane glass slides were used as substrates and cleaned with chromic acid followed by NaOH solution to remove the dirt, oil, etc., from the surface. The cleaned substrates were agitated with ultrasonic agitator using acetone and vapor degreased with isopropyl alcohol. Finally they were dried in an oven at 100 °C for 1 h before coating the thin films.

HAp/TiO_2 composite coating solutions with variable HAp/TiO_2 concentrations were prepared by mixing the required amounts of as prepared HAp and TiO_2 solutions. Six different HAp/TiO_2 concentrations were prepared in the present study. The mixed solution was diluted with 2-methoxy ethanol to make it suitable to deposit smooth films by dip coating. The deposited films were annealed at 500 °C for 1 h before doing further characterization.

2.2. Characterization

The structural and phase composition of the nanocomposites were qualitatively analyzed by XRD using Philips X'Pert Pro X-ray diffractometer with an operating voltage 40 kV and current 30 mA with high intensity Cu Kα radiation. A field emission scanning electron microscope (FESEM, JEOL JSM 6500) was employed to investigate the changes in the surface morphology of the nanocomposites with different HAp/TiO_2 concentrations. The distribution of elements on the surface of the films was evaluated by energy dispersive X-ray analysis (EDAX Genesis, FEI Co., Ltd.). The surface topography and the roughness were analyzed by atomic force microscope (AFM, Veeco, diCaliber). Roughness parameters such as R_a (average height above centre line) and R_{rms} (root mean square of R_a) were extracted from the AFM images. Different areas were scanned in the sample, and five sections for each area were measured to determine the mean roughness value. Nanoindentation was carried out (TriboLab™, Hysitron, INC) to study the mechanical strength and hardness of the nanocomposite coating with the maximum force and depth of 10 mN and 5 μm respectively. The films were tested at five different places in order to confirm the consistency in the mechanical strength. The mean values of the hardness and the elastic modulus was taken into account.

3. Results and discussion

3.1. X-ray diffraction analysis (XRD)

The XRD patterns for the HAp/TiO_2 nanocomposite films prepared with different concentrations are shown in Fig. 1. The XRD pattern for pristine HAp is shown in Fig. 1a. The characteristic diffraction peaks are in good agreement with HAp (JCPDS card #09-0432). The highly crystalline apatite peaks at 25.89°, 28.93°, 31.78°, 32.88°, 46.68° and 48.08° are the characteristic peaks of hexagonal HAp. Addition of 10 vol.% TiO_2 to HAp also shows (Fig. 1b) almost similar diffraction pattern like pure HAp with a small reduction in the intensity of HAp peaks. However a closer examination revealed the peak shift towards the lower angle, confirming the TiO_2 inclusion in HAp. In addition to the existing HAp

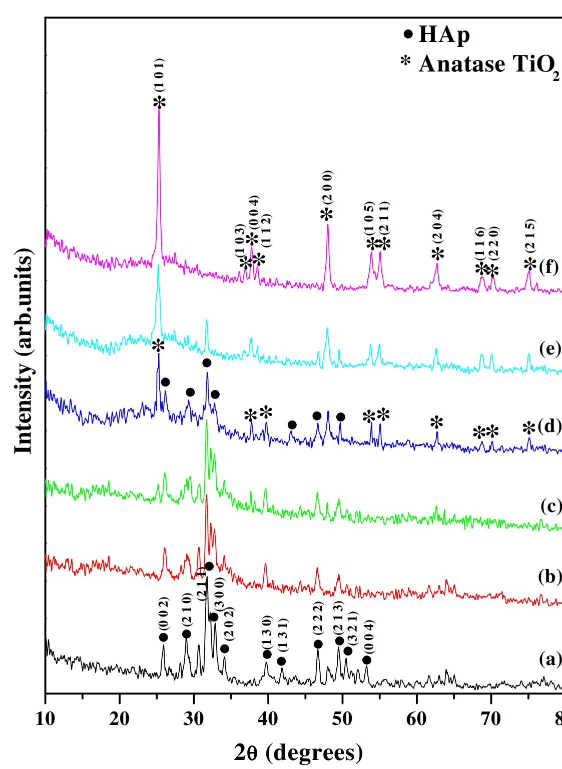

Fig. 1. XRD pattern of HAp/TiO_2 nano composite films (a) pure HAp, (b) 10 vol.% TiO_2, (c) 20 vol.% TiO_2, (d) 50 vol.% TiO_2, (e) 80 vol.% TiO_2 and (f) pure TiO_2.