Original research

Bioactivity analysis of the Ta (V) doped SiO₂–CaO–Na₂O–P₂O₅ ceramics prepared by solid state sintering method

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Abstract

The main objective of the study was to control the degradation rate of material at a higher degradation rate improving the chemical stability of the material. Ta is known to have good chemical resistance, biocompatibility and show no adverse biological response. In the present study, SiO₂–Na₂O–CaO–P₂O₅ bioceramics with different Ta₂O₅ contents was prepared by solid state sintering method at 1000 °C. The as-sintered ceramics were subjected to immersion studies in stimulated body fluid (SBF) for 21 days under static condition and characterized by XRD, FTIR, SEM, and AAS. The findings of the research indicate that the addition of Ta₂O₅ controlled degradability, and all samples showed sufficient bioactivity.

Keywords: Crystallization; Bioactivity; Ta₂O₅; Degradation rate; Bioceramic

1. Introduction

In 1920, bioceramic was first used for remodeling of damaged bone, and since then it has been considered as potential candidates for clinical use. The essential requirement for an implant natural or synthetic is high mechanical strength, corrosion resistance, biocompatibility, and the ability that any material not to create any toxic effect inside the body. Bioceramic has been selected as candidates for clinical use because its chemical composition stimulates with the mineral component of the bone [1–4]. Hydroxyapatite ceramic was discovered to hold direct bonding ability with both soft and hard tissues. This bone bonding ability makes ceramic more attractive for medical applications, especially to fill gaps and spaces of fractured bones, but it was observed that these materials descents in strength after a specific period of time [5]. It is required that the implant should have a substantial degradation rate so that it can be used for an extended period of time. Dissolution rate has greater importance in bioactivity, the higher dissolution rate increases the number of non-bridging oxygens (NBOs) resulting in an increase in reactivity. The Ta ions are considered to control degradability by providing chemical stability to the system. Tantalum being not part of human body acknowledged as inert material is considered to be a good candidate to be used as whole or part of implant material. It has sufficient biocompatibility and osteoconductivity, and exhibits good chemical resistance [6–8]. Tantalum has very little adverse biological response in either the reduced or oxidized forms [9]. Sharma et al. [10] reported that the presence of the oxide layer on tantalum enhances the absorption of protein at the interface and has highly corrosion resistive property. Some multivalent cations have the opposite effect on the bioactivity because they modify the chemical properties of the system and this depends on certain content. Srivastava et al. [11] reported that the transition metal oxides causes phase separation that in turn
modifies the structure. The present study aims to investigate the effect of Ta$^{+5}$ ions on bioactivity of SiO$_2$–CaO–Na$_2$O–P$_2$O$_5$ bioactive ceramic.

2. Experimental procedure

Hench Bioglass® [12] having chemical composition 46.1SiO$_2$–26.9CaO–24.4Na$_2$O–2.6P$_2$O$_5$ (mol%), which revealed excellent bioactivity [13] was selected as base composition. Five different compositions (given in Table 1) of bioceramics were formulated in this study with varying concentration of Ta$_2$O$_5$ in $(46.1-x)$SiO$_2$–26.9CaO–24.4Na$_2$O–2.6P$_2$O$_5$–xTa$_2$O$_5$ (where $x=0$, 0.1, 0.5, 1, and 3 mol%) system by solid state sintering method at 1000 °C temperature for the holding time of 4 h. The compacts ($\sim$15 dia) of as-sintered samples were prepared under hydrostatic pressure of 50 MPa. In vitro bioactivity test of samples were performed in SBF at 37 °C under static condition for 21 days. Phase composition of synthesized samples was studied using X-Ray Diffractometer Bruker, D-8 Advance, with a CuK$\alpha$ radiation ($\lambda=0.154$ nm, filter:Ni, voltage = 40 kV and current = 30 mA). International Center for Diffraction Data (ICDD) cards was used as a reference data for interpretation of peaks. Surface characteristics and surface morphology of samples were elucidated using Fourier transform infrared spectrometer, Midac, M2000 and scanning electron microscope, JSM- 6480VL, Joel, respectively. The test solution was also analyzed, and the variation in concentration of Si, Ca, P, Na and Ta was measured by Z-5000, Hitachi and changes in pH level by AD1111 pH meter.

3. Structural properties

3.1. X-Ray diffraction (XRD) analysis

The XRD patterns of all samples before and after soaking in SBF for 21 days are shown in Fig. 1(A and B) respectively. Wollastonite (CaSiO$_3$) was the main crystalline phase observed in all as-sintered samples, along with certain minor phases of whitlockite (Ca$_3$P$_2$O$_7$) and sodium calcium silicate ((Na$_2$Ca$_2$Si$_3$O$_9$), (Na$_2$Ca$_3$Si$_6$O$_16$)) were also observed (shown in Fig. 1A). This result is in agreement with the Mohamed Mami et al. [14]. The peak intensities of wollastonite (CaSiO$_3$) decreased with increase in Ta$_2$O$_5$ concentration. As non-bridging oxygen decreases with the increase in the concentration of Ta$_2$O$_5$ and the process of crystallization is affected[15]. Contrary to this, the whitlockite (Ca$_3$P$_2$O$_7$) phase appeared as the major phase in sample T5 having a higher concentration of Ta$_2$O$_5$. This is due to the property of Ta$_2$O$_5$ that it gives strength to the materials [16]. The phase of (Ca$_3$P$_2$O$_7$) appeared as a new phase in this research as compared to the XRD pattern of the research paper which is followed. This indicates that with the addition of Ta$_2$O$_5$ in the present research the strength of the sample increased.

After immersion in SBF: All the samples exhibit abundant of hydroxyapatite (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$) phases, which is due to the formation of a crystalline layer on all the samples. The hydroxyapatite (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$) phase appeared as the main crystalline phase with major peak intensity except in sample T5, as shown in Fig. 1(b). In the samples containing lower Ta$_2$O$_5$ concentration, the excess of non-bridging oxygen increases the apatite formation.

The phases of wollastonite (CaSiO$_3$), whitlockite (Ca$_3$P$_2$O$_7$) and sodium calcium silicate ((Na$_2$Ca$_2$Si$_3$O$_9$), (Na$_2$Ca$_3$Si$_6$O$_16$)) diminished in all samples except in sample T5. In sample T5,
the hydroxyapatite phase was observed as a minor phase due to higher amount of Ta$_2$O$_5$ which decreases the ability of apatite crystal formation. The phases of wollastonite (CaSiO$_3$) and sodium calcium silicate (Na$_2$Ca$_3$Si$_6$O$_{16}$) appeared as the major phases in the sample T5. The more intense and sharp peak of hydroxyapatite (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$) appeared in the sample T1 because it is more bioactive as shown in the XRD pattern. The crystalline phases could be indexed with wollastonite (CaSiO$_3$)
(JCPSD Card no. 074-0874), whitelocke (Ca$_3$(PO$_4$)$_2$ (JCPSD Card no. 009-0169), sodium calcium silicate (Na$_2$Ca$_2$Si$_3$O$_9$), (JCPSD Card no. 022-1455), (Na$_2$Ca$_3$Si$_6$O$_{16}$)(JCPSD Card no. 023-0671) and hydroxyapatite (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$)(JCPSD Card no. 022-1455). This result is in accordance with the Fernandes et al. [17].

4. Optical properties

4.1. Fourier transform infrared (FTIR) transmission

4.1.1. FTIR before immersion in SBF

The Fourier transform infrared transmission spectra (FTIR) of ceramic samples before and after immersion in simulated body fluid (SBF) for 1, 3, 7, 15 and 21 days are shown in Fig. 2(A, B, C, D, E and F) correspondingly. The transmittance spectra in Fig. 2(A) before soaking, of all the ceramic samples appeared at 1406.8 cm$^{-1}$ in simulated body fluid shows the peak of Si–O–Si stretching of non bridging oxygen atoms at about 949.9 cm$^{-1}$ and at 1033 cm$^{-1}$, and the peak of Si–O–Si Tetrahedral at about 784.3 cm$^{-1}$. The peak of phosphate band occurred at 563.1 cm$^{-1}$ and of Hydroxyl bands appeared at about 1635 cm$^{-1}$ and 3419.4 cm$^{-1}$. The peak of carbonate band appeared at 1406.8 cm$^{-1}$. This result is due to the presence of large amounts of silica and small amount of phosphorous in our ceramic composition. The above result is in accordance with the ASrivastava et al. and Fernandes [18,19].

4.1.2. FTIR after immersion in SBF

- **After 1 day** the peaks of silicate bands of all the samples were shifted from 949.9 cm$^{-1}$ to 951.5 cm$^{-1}$ and the peak at 1033 cm$^{-1}$ shifted to 1036.4 cm$^{-1}$ respectively. The peak at 784.3 cm$^{-1}$ disappeared. The new amorphous peak of phosphorous band occurred at 564.5 cm$^{-1}$ and peak of the carbonate band at 1406.8 cm$^{-1}$ disappeared in all the samples after 1 day.

- **After 3 days** the peak of the silicate band at 1036.4 cm$^{-1}$ shifted to 1044.3 cm$^{-1}$ and this peak became intense, showing clearly the formation of a silica rich layer. The peak of phosphate band shifted to about 562.4 cm$^{-1}$, and the new peak of phosphate band appeared at 1074.5 cm$^{-1}$ in all the samples showing the growing hydroxyapatite (HAP) layer. As stated before, the series of reactions in SBF is such that the silicon oxide released into the solution and silica layer formed on the surface of the material. Silica rich layer acted as the nucleation sites for the calcium phosphate rich layer.

- **After 7 days** the new peak of carbonate appeared at 787 cm$^{-1}$, the peak of phosphate band shifted to 1089.9 cm$^{-1}$ and no other significant changes occurred.

- **After 15 days** the P–O band shifted to 1099.8 cm$^{-1}$, the silicate band shifted to about 1043.1 cm$^{-1}$, the new carbonate band appeared at 1419.2 cm$^{-1}$ and the crystalline phosphate band appeared at 550 cm$^{-1}$ in all the samples.

- **After 21 days** the carbonate band at 1419.2 cm$^{-1}$ shifted to 1400.2 cm$^{-1}$, the phosphate band at 1049.8 cm$^{-1}$ shifted to 1053.6 cm$^{-1}$, the silicate band disappeared, the Hydroxyl bands shifted to 1621.4 cm$^{-1}$ and 3433.8 cm$^{-1}$. The crystalline phosphate band shifted at 548 cm$^{-1}$ in all the samples, and all these peaks became intense, which shows clearly the formation of hydroxyapatite (HAP) layer on all the samples. Above mentioned result is in accordance with the Mezahi et al. [20].

The result of FTIR (described in Table 2) illustrates that all the samples showed bioactivity, the bioactivity remains the same for a small amount, but as the amount of Ta$_2$O$_5$ increased the bioactivity decreased. These results are in accordance with the XRD patterns.

5. Surface properties

5.1. Scanning electron microscopy (SEM) analysis

The SEM images of samples T1, T2, T3, T4 and T5 before and after immersion in SBF of 3rd, 7th and 21th day are shown in Fig. 3.

From these images, it is clearly perceived the formation of hydroxyapatite (HAP) layer after immersion in simulated body fluid. The images of SEM before immersion show no apatite crystals and after soaking in simulated body fluid (SBF), the ceramic surface is fully covered with crystals of apatite with only few pores. There are various grains of unequal shapes and sizes on the surface of the ceramic samples. In accordance with the other results the sample T1 was most bioactive and it shows apatite crystals more than the other samples. Then the grains of the samples reduced as the concentration of Ta$_2$O$_5$ increased and very few grains appeared in sample T5. As Ta$_2$O$_5$ act as a network modifier, but when its concentration is higher it behaves like a network former. The network former decreased the non-bridging oxygen and consequently decreased the ability to form the crystals of apatite. The consequences of apatite formation from SEM images were similar to the previous results of FTIR and XRD. These results of SEM images are in good accordance with the Camillo et al. [21], Alemany et al. [22] and Enobong et al. [1].
6. Chemical properties

6.1. Atomic absorption spectroscopy (AAS) analysis

The determination of Si, Ca, P, Na and Ta ions in simulated body fluid (SBF) for different time intervals are shown in Fig. 4(a), (b), (c), (d) and (e).

The silicon concentration in SBF increased rapidly due to rapid released of silicon ions in SBF. The silicon ions in SBF formed silanols (Si–OH) at the surface of ceramics and then it helped in the formation of a silica rich layer on the surface. This acted as a nucleating agent for the formation of calcium phosphate layer on ceramic sample.

The calcium concentration graph indicates three stages. In the first stage the ion concentration of calcium increased, in the second stage it became stable for a very short interval, and then from 15 to 21 days a significant decrease occurred. This means that calcium ion dissolution reaction completed in the earlier stage then the process of formation of HAP layer started from 15th day, thus a decrease was observed in the last stage, showing the requirement of calcium ions in deposition of calcium rich phosphate layer. The concentration of calcium in simulated body fluid also shows the presence of calcium ions in SBF in large amount.

The phosphorus concentration decreased with the increase in silicon concentration, showing the formation of hydroxyapatite.
layer on the surface of ceramic samples. This shows the incorporation with the calcium ions to form calcium phosphate layer on the surface of the material.

The sodium concentration increased in the SBF as shown in Fig. 4(d). The sodium ions dissolved in simulated body fluid rapidly, which increased the supersaturation of the solution and

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Fig. 4. Variation in concentration of Si (a), Ca (b), P (c), Na (d) and Ta (e) in test solution with reaction time.
consequently it was very significant in the formation of apatite layer. These results are in good agreement with the Hofmann et al. [23].

The concentration of tantalum increased in the start and decreased slightly as shown in Fig. 4(e). This decrease is due to the reason that tantalum oxide also acts as a nucleating agent for the calcium rich phosphate layer [24]. After that, this concentration again increased, then decreased as illustrated in Fig. 4(e). This behavior is due to the fact that tantalum oxide supports in the formation of hydroxyapatite layer on the samples. The straight line in the graph shows absence of tantalum concentration in the sample T1. This result is in accordance with the Pyare et al. [18].

6.2. Weight loss measurements

The weight loss of the samples as a function of reaction time is shown in Fig. 5. This measurement of the samples indicates the dissolution behavior of the samples and gave the perception about how much sample was dissolved in SBF. The graph in Fig. 5 illustrates that the weight loss of all the samples increased with the increase in soaking time until 15th day but after that no significant change occurred. This means that ion exchange reaction completed till the 15th day, then the process of deposition of hydroxyapatite (HAP) layer started, thus the requirement of ions was reduced which in turn displayed no significant change in the weight loss after 15 days. This indicates the formation of a HAP layer on the samples and is in consent with the other results. It can also be seen that as the concentration of tantalum oxide (Ta2O5) increased, the chemical durability of samples increased and displayed minor weight loss. It has been found that the sample T1 was less durable than all the samples and it showed a higher weight loss. This result is in accordance with the Qianbin et al. [25].

6.3. pH measurements

The pH of the samples after soaking in simulated body fluid (SBF) as a function of soaking time is shown in Fig. 6. The pH measurements were made to know the dissolution behavior of the samples in SBF. The pH of the samples increased at the start. Then the deposition of calcium phosphate layer caused no significant change in pH value in the later time period. The Ta2O5 increased the stability and strength of the samples and so it reduced the dissolution rate of the samples [16]. The less durable sample dissolved more as illustrated in weight loss measurement, from which the pH of the solution increased. Fig. 6 illustrates that sample T1 had pH value more than the other samples as a consequence of tantalum oxide concentration absence. As compared to sample T1, sample T5 had a low pH value. The pH results are in consent with the weight loss result as described. The variation of pH shows the formation of apatite layer. This result is in good agreement with the Essien et al. [1].

7. Conclusion

In the present study, Ta(V) doped SiO2–CaO–Na2O–P2O5 ceramics was prepared by conventional solid state sintering method. In vitro assays were performed in order to determine the effect of Ta2O5 on degradability rate and bioactivity of the ceramic bodies. The result indicates that Ta^{+5} ions controlled degradation rate of the system and improved the stability of bioceramics. A controllable degradation of bioceramic can be achieved with an optimized amount of Ta2O5 that makes it suitable for clinical use for an extended period of time.

References


