Processing and Characterization of Titanium–Tricalcium Phosphate Metal Matrix Composite for Biomedical Applications

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Abstract

Titanium-tricalcium phosphate (Ti-TCP) metal matrix composites are one of the best biomaterials that have attracted significant attention in recent years. These composites consist of a titanium matrix reinforced with tricalcium phosphate (TCP) particles, which imparts improved mechanical and biological properties. The unique properties of Ti-TCP composites make them suitable for use in various biomedical applications such as dental and orthopaedic implants. The processing of Ti-TCP composites involves several techniques such as powder metallurgy, hot pressing, and sintering.

In this work, powder metallurgy method is used for the production of Ti-TCP composites. In this method, the powders of Ti and TCP are mixed together in a ball mill to obtain a homogenous mixture. The mixture is then compacted into a desired shape and sintered at high temperature and pressure. In this process we prepared three samples of Ti and TCP by varying the weight ratio and these samples are characterized by techniques such as microstructural analysis, mechanical testing, and biocompatibility testing. Microstructural analysis using scanning electron microscopy (SEM) and X-ray diffraction (XRD) reveals the morphology and distribution of the Ti and TCP particles in the composite. Mechanical testing such as Density and compression testing evaluates the mechanical properties of the composite. Biocompatibility testing involves in vitro to assess the biocompatibility, osteointegration, and biodegradation properties of the composite.

Keywords: Biocompatibility, orthopaedic implants, SEM, Titanium, Tricalcium phosphate, XRD

1. Introduction

Ageing and accidents are the two primary causes of bone degradation, damage, and disease. Even though bone tissue can grow and develop, there are some critical illnesses and circumstances where it cannot. The best practical answer to this problem is vaccination. Autografts, allografts, and synthetic grafts are the three fundamental methods for replacing missing bone or treating bone defects. Application is hampered by a lack of bone donors and additional traumas, similar to autografts and immune system-unaffected. Numerous ceramic and metallic tissues are designed to aid in bone regrowth and bone healing. In a biological setting, biomaterials—which might be organic or inorganic—behave like harmed tissues. Biomaterials must have excellent bioactivity and biocompatibility. Among other things, it should have traits in common with broken or injured bones. High corrosion and wear resistance is also significantly influenced by the biomaterials used in cargo. Metallic biomaterials are preferred in stack bearing orthopaedic inserts due to their superior mechanical characteristics. Biomaterials that are of good quality and have a respectable level of erosion resistance are used in the production of orthopaedic inserts. Because they can survive the severe mechanical loading that takes place inside the human body, these materials are favoured. Researchers have focused a lot of attention on metallic biomaterials, but more research is required to better understand characteristics including malleability, Youngs' modulus, weakness break, push protecting, wear and erosion resistance, biocompatibility, and bioactivity. At the moment, titanium and its combinations, magnesium and its amalgams, cobalt chromium (Co-Cr) amalgams, 316L stainless steel (316LSS), and calcium phosphate ceramic are utilised to make surgical inserts. The development of titanium-tricalcium phosphate in the realm of biomaterials has come later.

2. Material

2.1 Titanium and Tricalcium Phosphate MMCs:

A type of composite material known as titanium-tricalcium phosphate metal matrix composite (Ti-TCP MMC) is composed of a titanium (Ti) metal matrix with reinforcing tricalcium phosphate (TCP) particles. The TCP particles typically appear as fibres, whiskers, or particles. By combining the advantages of titanium and TCP, the Ti-TCP MMC creates a substance with enhanced mechanical and biological qualities. Titanium is an excellent metal for implants and other medical devices because it is strong, lightweight, corrosion-resistant, and has outstanding biocompatibility. On the other hand, tricalcium phosphate is a biocompatible ceramic substance that is frequently utilised in bone transplants due to its capacity to stimulate bone formation.

The biological and mechanical properties of the composite material can be considerably enhanced by including TCP particles into the titanium matrix in a Ti-TCP MMC. The TCP particles can improve the material's biocompatibility, fostering bone development and tissue integration. The TCP particles can also enhance the composite material's mechanical qualities, boosting its strength and toughness.

In contrast to conventional materials, Ti-TCP MMCs can offer superior biocompatibility and mechanical qualities in a number of medical applications, including orthopaedic and dental implants. Their special combination of properties can offer advantages over conventional materials in other applications like aerospace, automotive, and sporting goods.

2.2 Preparation of Ti-TCP MMCs:

Titanium-tricalcium phosphate metal matrix composites (Ti-TCP MMCs) can be made in a variety of ways, such as:

➢ Powder metallurgy: In this technique, Ti and TCP powders are combined, the resulting mixture is pressed into the proper shape, and the finished compact is then sintered in a high-temperature furnace. The Ti and TCP particles combine during sintering to create a metal matrix composite.

➢ With in situ synthesis, the titanium matrix is combined with a TCP precursor, such as calcium phosphate, and heated in a high-temperature furnace. A Ti-TCP MMC is created when the titanium and TCP precursor react during heating to produce TCP particles inside the metal matrix.

➢ Solid State Reaction: In this procedure, particles of Ti and TCP are combined, and the resulting mixture is heated in a high-temperature furnace. The Ti and TCP particles interact during heating to create a metal matrix composite.

➢ Reactive infiltration: In this technique, molten Ti is brought into contact with a preform made of a porous ceramic material, such as TCP, and infiltrates the preform to create a Ti-TCP MMC.

The final product's intended qualities and the particular application for the composite material determine the preparation process to be used. Each technique has advantages and disadvantages of its own, and the choice of the best technique depends on elements like cost, complexity, and scalability.

3. Methodology

In this paper we used Powder Metallurgy technique for the preparation of Ti and TCP metal matrix composite. The following flow chart shows the actual process.

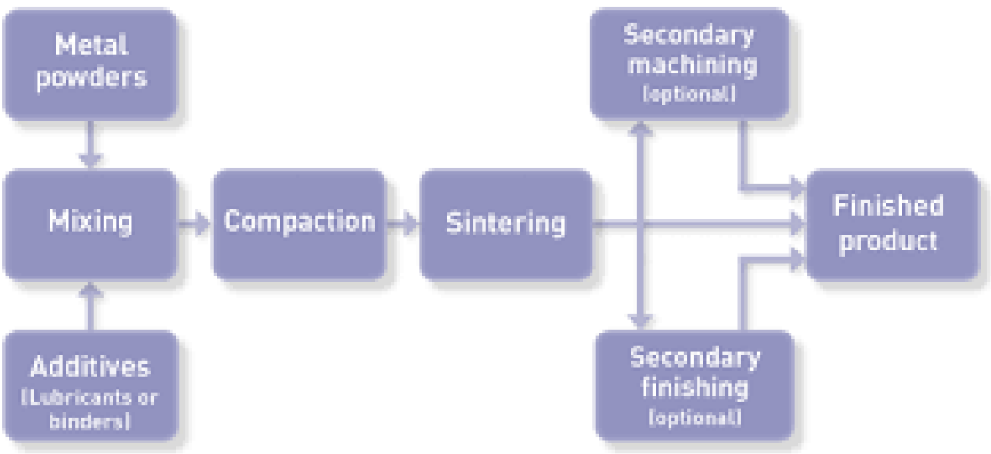

Figure 1: Powder Metallurgy Process

Powder metallurgy is a manufacturing process used to produce parts and components from metallic powders. The process involves the following steps:

➢ Blending or Milling

➢ Pressing or Compacting

➢ Sintering

3.1 Ball Milling:

A revolving cylindrical container packed with metal balls is used in the mechanical process known as ball milling to reduce the size of the material being processed. The material is broken down into smaller pieces as a result of the balls' collision and crushing of the substance. Due to its ability to produce fine materials, this process is frequently used in the manufacturing of ceramics, drugs, and other items and uniform powders. Ball milling can also be used to combine materials since the grinding medium evenly distributes and mixes the constituent parts.

Additionally, it can be used for the synthesis of new materials through reactions that occur during milling. The length of the milling time and the size of the milling balls can affect the size and homogeneity of the final product.

3.2 Compaction:

Powder metallurgy uses the compaction process to shape metal particles into the required shape. Using a mechanical press, the procedure entails exerting pressure on the powder particles contained in a die or mould. The press could be electric, mechanical, or hydraulic. The powder particles attach to one another when pressure is applied, creating a solid shape. The compressed shape is then taken out of the mould and is prepared for the following stage of powder metallurgy, which might include sintering or other auxiliary operations. Simple cylindrical or rectangular shapes, as well as more complex shapes with interior characteristics, can all be produced using the compaction process. By altering the pressure and the size of the powder particle, the compacted part's density can be managed.

3.3 Sintering:

In order to create a solid mass, a compacted or shaped powder material is heated to a temperature below its melting point by the process of sintering. A material that is denser, stronger, and more homogenous in composition than the beginning powder is created during the process by heating the powder particles to a temperature where they fuse together. Heating, maintaining at a given temperature for a predetermined amount of time, and cooling are some of the steps in the sintering process. The particular material that is being sintered and the desired qualities of the finished product determine the precise process variables, such as temperature, time, and environment. Sintering is a crucial stage in many powder metallurgy processes and is frequently employed in the manufacturing of ceramics, metals, and composites.

4. Synthesis of Ti and TCP MMCs

Titanium powder is mixed with Tricalcium Phosphate TCP. The powders were mixed in varying percentage of weight ratio as shown in the table 1.

Sample code	Weight% of TI	Weight% of TCP
Ti	100	0
Ti20	80	20
Ti25	75	25

Table 1: Sample Composition

4.1 Sample Preparation

The Ti and TCP powders were combined in accordance with their respective percent weights, as given in Table 1, and then ball milled for 6 hours in a planetary ball mill. The wetting medium employed was ethanol. Stainless steel balls and stainless-steel vials were used in the ball milling process, and the 20:1 ball to powder mass ratio was maintained. Ball milling was carried out at 400 rpm in 15-minute cycles, with a subsequent 15-minute rest period. This cycle was repeated for a total of 8 hours of milling time. The particles from the milling process were compressed using a 15 mm diameter die and a 10-tonne load in a uniaxial single action hydraulic compaction machine. The lubricant used was zinc stearate. The green compact was then sintered for 35 minutes at 800°C in a muffle furnace using normal air and 200°/min was the chosen heating rate.

4.2 Sample characterization

On abrasive silicon carbide paper of grades 1 to 4, the sintered samples were polished. The samples were ultrasonically processed in acetone for 15 minutes after being washed in distilled water. SEM and XRD were used to characterise the milled and sintered samples as-is for morphology and phase contamination. The XRD scanning range was 20° to 60° with a 3°/min step size.

4.3 In-vitro bioactivity study of samples in SBF

The polished samples were cleaned using an ultrasonic cleaner for 15 minutes with acetone and distilled water. For two weeks, the samples were allowed to soak in freshly made SBF. The SBF is a solution that has an ion concentration similar to that of human blood plasma and is maintained in mild pH and physiological temperature settings. By adhering to Kokubo's approach, SBF was created. By adding 1.0 M HCl, the pH of the final sample was changed to 7.42. SBF was kept in a sanitary container and kept at 4°C in the fridge. A 50 ml plastic falcon tube containing 50 ml SBF was used to store each sample.

4.4 Density Measurement and Compressive Strength Testing

We tested the 3 samples for compressive strength using universal testing machine in the laboratory and density is measured.

5. Results

5.1 Sem Results

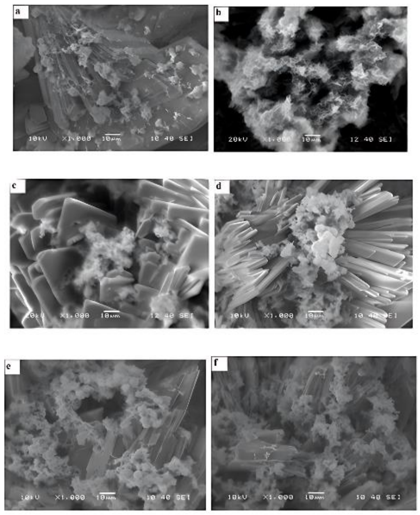

Figure 2: SEM micrographs of ball milled and sintered composites in SBF. (a) Ti, for 1 week (b) Ti, for 2 weeks (c) Ti20, for 1week (d) Ti20, for 2 weeks (e) Ti25, for a week (f) Ti25, for 2 weeks.

Figure 2 shows the SEM micrograph of samples with different Ti-TCP% wt. ratio soaked in SBF for 1 and 2 weeks. Fig.2a shows the microstructure of Ti soaked in SBF for 1 week. It was observed that globular apatite particles have been deposited on the sample and more globular apatite was deposited after 2 weeks of immersion (Fig.2b). Fig.2c shows the surface of Ti20 samples where more globular apatite was observed when compared to Ti samples. Increasing the immersion time leads to the nucleation of more apatite particles. Fig.2e shows the micrograph of Ti25 samples. The surface of Ti25 is covered with more globular structure as compared to Ti and Ti20 samples. Also, Ti25 sample soaked for 2 weeks showed more apatite nucleated. A thick layer of apatite can be seen on Ti25 surface soaked in SBF for 2 weeks of immersion (Fig. 2f). With the increase of immersion time, more apatite deposits and their size grew gradually forming dense apatite layer.

5.2 XRD PATTERNS

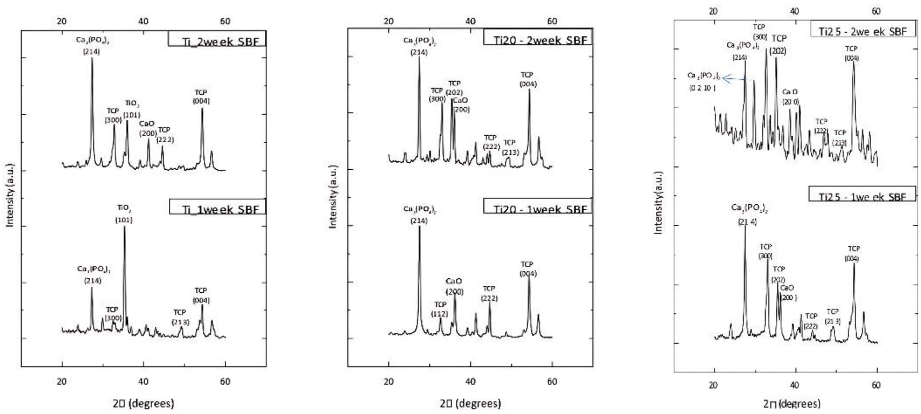

Fig 3: XRD pattern of Sintered samples Ti, Ti20, Ti25 composite in SBF for 1 and 2 weeks

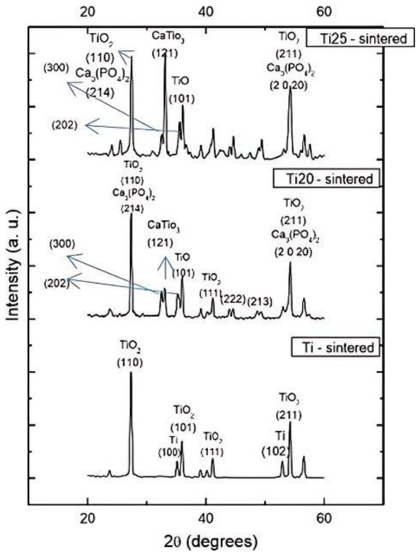

Fig 4: XRD patterns of 3 Sintered samples

- Sintering of Ti-TCP samples at 900°C resulted in the formation of titanium oxide (TiO2) peaks, including the rutile phase, as well as the creation of CaTiO3 through the reaction between Ti and TCP. The presence of Ca3(PO4)2 phase and increasing TCP peaks indicated further TCP breakdown.
- After one week of solubilization in SBF, sintered Ti samples developed apatite on their surfaces, with Ti25 samples exhibiting thicker apatite coatings than pure Ti samples.
- In Ti20 and Ti25 samples, longer soaking times resulted in higher TCP peaks and smaller TiO2 peaks, indicating improved TCP deposition and coverage of Ti surfaces.
- Higher TCP content led to increased TCP intensity and distribution as well as more apatite development, according to a comparison of Ti, Ti20, and Ti25 samples. Longer soaking times resulted in apatite layer thickening, as seen in SEM pictures.

6.Mechanical Testing

6.1 Density Test:

The Archimedes principle was used to determine the samples' densities. The findings of the density measurement using both the Archimedes approach and a theoretical density estimate are shown in Table 2. The findings indicated that as the concentration of hydroxyapatite increased, the density dropped. In comparison to a ball-milled pure Ti sample, the relative density of Ti20 was found to be 99%, while that of Ti25 was found to be 94%.

Sample Code	Density (gm/cc)	Theoretical Density (gm/cc)
Ti	3.238	3.267
Ti20	3.221	3.121
Ti25	3.050	3.107

Table 2: Density Measurement

6.2 Compressive Strength Test

Mechanical properties of Titanium-TCP composites are evaluated using a universal testing machine does it the results are shown in table 4 the composite with 20% TCP content exhibited the highest compressive strength of 652.5Mpa which is 25% greater than the pure titanium.

Sample	Compressive strength
Ti	522
Ti20	652.5
Ti25	609.73

Table 3: Compressive strength

7. Advantages

➢ **Enhanced mechanical properties:** Compared to pure titanium, Ti-TCP MMCs have stronger, harder, and more fracture-resistant properties, making them appropriate for load-bearing applications in bioengineering.

➢ **Bioactivity and biocompatibility**: TCP increase association with surrounding bone tissue and encourages the creation of a hydroxyapatite layer. Excellent biocompatibility makes both titanium and TCP less likely to cause adverse responses or tissue rejection.

➢ **Osteoconductivity and bone regeneration:** Ti-TCP MMCs support the development of bone tissue by promoting bone cell adhesion, proliferation, and differentiation. They also promote Osteoconductivity.

➢ **Corrosion resistance:** Titanium's superior capacity to withstand corrosion enables the long-term stability and toughness of Ti-TCP MMCs when they are implanted, maintaining the structural integrity of implants and limiting negative effects on surrounding tissues.

8. Limitations

➢ **Processing difficulties:** Fabricating Ti-TCP MMCs can be difficult and necessitate the use of specialised tools and methods. It can be difficult to distribute TCP particles uniformly throughout the titanium matrix, which could result in differences in the material's characteristics.

➢ **Thermal expansion mismatch:** Tricalcium phosphate (TCP) and titanium have differing thermal expansion coefficients, which results in a thermal expansion mismatch. At the interface between the titanium matrix and TCP particles, this mismatch may lead to stress build up and eventual material failure, especially during thermal cycling or temperature fluctuations.

➢ **Degradation and Resorption:** TCP is a bioresorbable substance that can deteriorate over time inside the body. Although this characteristic may be helpful in some situations, it may have a negative impact on the structural integrity and long-term stability of Ti-TCP MMCs, particularly in load-bearing situations where a more permanent implant is required.

➢ **Limited load-bearing ability:** Ti-TCP MMCs may still be constrained in terms of load-bearing capacity while having better mechanical characteristics than pure titanium. Alternative materials or composite designs might be better appropriate for applications that need great mechanical strength and resilience to wear and fatigue.

9. Applications

➢ **Orthopaedic implants:** Ti-TCP MMCs are employed in the creation of orthopaedic implants like bone plates, screws, and joint replacements. These composites provide enhanced mechanical, bioactive, and biocompatibility qualities that encourage better integration with the surrounding bone tissue and increase the stability of the implants over the long term.

➢ **Bone graft substitutes:** Ti-TCP MMCs are used as bone graft alternatives in situations when bone regeneration is necessary. TCP's osteoconductive characteristics help promote the growth of new bone tissue, which promotes the repair and reconstruction of bone fractures or deformities.

➢ **Scaffolds for tissue engineering:** Ti-TCP MMCs are used in tissue engineering applications as scaffolding materials. They offer a three-dimensional framework that encourages cell adhesion, growth, and differentiation. Ti-TCP MMCs are appropriate for tissue engineering of bone and cartilage because of the bioactive nature of TCP, which encourages cell adhesion and tissue formation.

➢ **Dental implants:** Ti-TCP MMCs are used in dental implants because they offer bioactivity and mechanical strength. TCP integration improves osseointegration, improving implant stability and extending the useful life of dental implant operations.

➢ **Drug delivery system:** Ti-TCP MMCs may be employed as carriers in systems for the controlled delivery of drugs. The composite's porous nature allows therapeutic chemicals to be loaded and released, making it ideal for targeted drug administration for bone-related treatments or regenerative therapies.

10. Conclusion

➢ The production of Ti-TCP composite using powder metallurgy with high-energy sintering and ball milling methods was successful.
➢ Ti25 composite showed a higher volume fraction of pores compared to other sintered samples, which also had a more porous structure and more TCP content.
➢ TCP partially disintegrated during sintering at 800°C. Ti and TCP then interacted to generate $CaTiO_3$, which aided in the production of apatite.
➢ The presence of $Ca_3(PO_4)_2$ and TiO_2, which were beneficial for the synthesis of apatite, was discovered using XRD analysis.
➢ When submerged in simulated bodily fluid for a week, Ti-TCP composite demonstrated superior bioactivity to pure Ti, and TCP deposition increased with larger TCP content.
➢ Mechanical tests revealed a maximum compressive strength of 652.5 MPa for the Ti-TCP composite with a 20% TCP concentration, which is 25% more than pure titanium.
➢ With Ti20 composite having a relative density of 99% and Ti25 composite having a relative density of 94% compared to a balled-up pure Ti sample, density measurements showed a decrease in density with increasing TCP content.

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