Fracture Mechanism of Interpenetrating Iron-Tricalcium Phosphate Composite

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Abstract. The usage of iron alloys for bone fractures treatment has been limited due to its high density and elastic modulus, as compared to bone. In contrast, the use of tricalcium phosphate (TCP), a ceramic that promotes bone healing, is mostly limited by its brittle nature. In the present work the fracture mechanism of a novel iron-TCP interpenetrated composite fabricated by spark plasma sintering was studied. Specimens were subjected to a diametral tensile-strength-test. The work of fracture was determined by indirect tensile loading conditions using the diametral tensile strength test. The results revealed that iron has a clear toughening effect on the microstructure of tricalcium phosphate specimens consolidated by spark plasma sintering. This is a promising result to overcome the limited usage of tricalcium phosphate to treat only non-load bearing bone defects.

Introduction

Recently new type of composite material with promising properties suitable for the fabrication of osteosynthetic devises has been developed. This new material is composed by iron and tricalcium phosphate powders and was consolidated by spark plasma sintering [1]. The rationale behind this formulation is that iron can increase the fracture toughness of tricalcium phosphate without compromising the biocompatibility of this ceramic. This work was focused to determine the work of fracture of this new composite to validate the former hypothesis.

The diametral tensile-strength-test was applied to determine the work of fracture of the composite under indirect tensile conditions [2, 3]. This method has the advantage of being applied to geometrically simple shape samples, which can be easily fabricated by spark plasma sintering.

Materials and methods

Tricalcium phosphate powder was prepared by solid state reaction between a stoichiometric mixture of $CaCO_3$ (Sigma-Aldrich C4830) and $CaHPO_4$ (Merck 102304) at 1100 °C according to the following reaction.

$$CaCO_3 + 2\,CaHPO_4 \rightarrow Ca_3(PO_4)_2 + CO_2 + H_2O \quad (1)$$

Afterwards, the sintered block was milled (Fritsch Pulverisete 6) in isopropanol at 400 rpm using agate jar and balls (20 balls of 20 mm in diameter). Tricalcium phosphate powder was mixed with different volumetric amounts (between 0 and 50 %) of iron powder (Applied Carbon Nano

Technologies). The mixtures were homogenized and then consolidated at 1000 °C by spark plasma sintering (Dr. Sinter 1050 system) applying a direct current of 600 A at 3 V, in on-off cycles of 12 and 2 ms (heating rate of 150 °C/min). Samples (12 mm in diameter and 6 mm thickness) were sintered for 10 min applying a constant uniaxial compaction load of 35 MPa. The μCT analysis was conducted using the GE phoenix *v*|tome|*x* L 240 system equipped with a 180 kV/20 W maximum power nanofocus X-ray tube and high contrast flat panel detector DXR250.The skeletal densities of the samples were determined by helium pycnometry (AccuPyc II 1340, Micromeritics).

Diametral tensile-strength-test was performed in a TIRA test 2850S universal testing machine, using actuator velocity of 1 mm/min until fracture. At least 4 samples of each composition were used in order to define possible measurement errors. The work of fracture (γ_{wof}) was obtained from the area below of the obtained load P versus actuator displacement d curves, divided by the total projected surface area A of the two obtained fracture surfaces, Eq. 2.

$$\gamma_{wof} = \frac{\int_0^{\mathrm{d}_{fracture}} P \, \mathrm{dd}}{2A} . \qquad (2)$$

The area below the P versus d curve was numerically integrated applying the trapezoidal rule.

$$\int_0^{\mathrm{d}_{fracture}} P \, \mathrm{dd} \approx \frac{\mathrm{d}_{fracture}}{2\,N} \sum_{i=1}^{N} (P(\mathrm{d}_{i+1}) + P(\mathrm{d}_i)) , \qquad (3)$$

where $\mathrm{d}_{fracture}$ is the actuator displacement when fracture occurred.

The appearance of the fracture surfaces was observed by scanning electron microscope (TESCAN Lyra3) on samples previously coated with thin carbon layer to prevent charging during observation.

Results and discussion

Samples were systematically fabricated by spark plasma sintering method. Samples prepared with no iron addition presented the typical white color of calcium phosphate ceramics, while samples containing iron presented dark grey metallic aspect. X-ray computed micro-tomography showed that the two components form a continuous three-dimensional network in the material (Figure 1). The samples developed a good degree of densification as their surfaces presented bright appearance. Furthermore, the measured density of the samples was above 95 % of their theoretical density, determined by considering the volumetric fraction of their components.

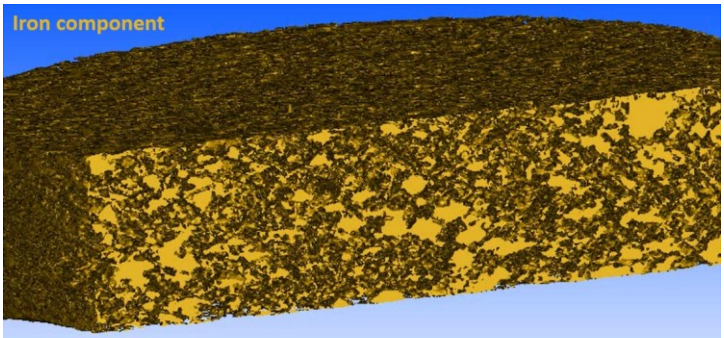

Figure 1. Tomographic reconstruction, showing an internal plane in the iron-TCP composite. The image only shows iron position, while the TCP was virtually removed for clarity.

All samples disclosed brittle fracture behavior during the diametral tensile-strength-test. Just as shown in Fig. 2, the fracture propagated longitudinally through the diameter of the specimens, between the points where the load was applied. Representative scanning electron microscope images of the fracture surfaces are included in Fig. 3. Both, pure tricalcium phosphate and the iron-tricalcium phosphate composites, presented brittle fracture surface, *i.e.* without evidence of plastic deformation. Besides, iron particles were not detached from the surface, suggesting good interphase adhesion. While tested by means of compression test, iron exhibited ductile fracture while intergranular decohesion was observed for TCP areas.

Figure 2. Representative image of the fracture of the spark plasma sintering samples, after the diametral tensile-strength-test.

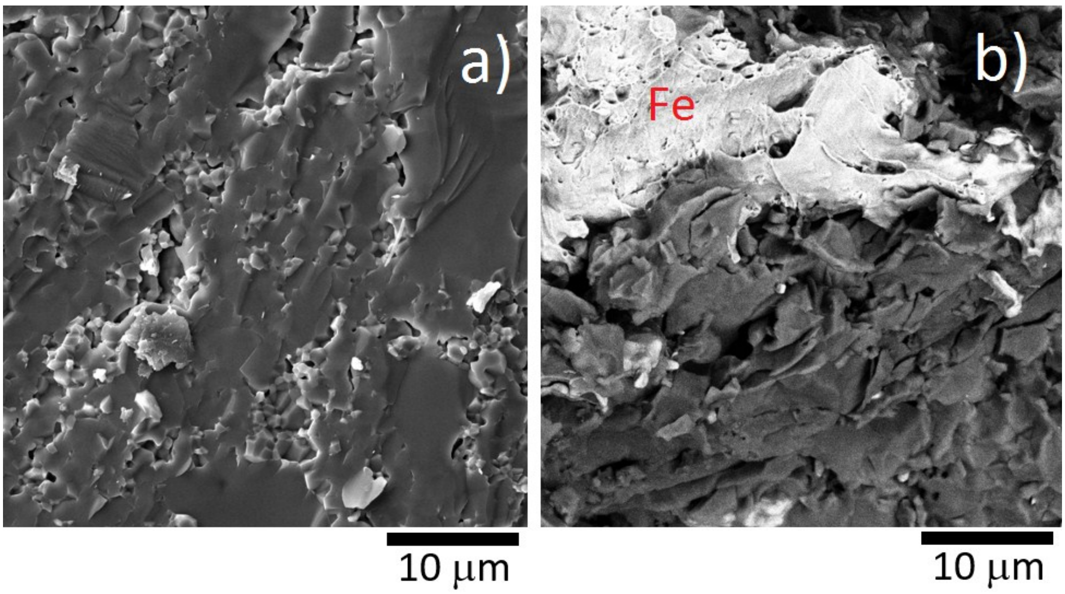

Figure 3. Representative scanning electron microscope images of the fracture surface of a) pure tricalcium phosphate and b) 50 volume % iron – tricalcium phosphate composite, consolidated by spark plasma sintering. Fe indicates the position of iron in the composite fracture surface.

Fig. 4 shows the γ_{wof} determined for the studied samples. Results show a positive correlation between γ_{wof} and iron content. The linear regression indicates a correlation factor R^2 of 0.96. This fact suggests that the incorporation of iron promotes the toughening of the microstructure of tricalcium phosphate consolidated by spark plasma sintering. The possible toughening mechanisms include grain bridging, crack deflection or microcracking [4]. Although the specific toughening mechanism was not yet determined, the improved fracture toughness of tricalcium phosphate has relevant implications. For example, the application of tricalcium phosphate to treat bone defects is limited by its brittle mechanical behavior [5], therefore, the addition of iron, a metal well tolerated by the human body [6], can extend the use of tricalcium phosphate to load bearing conditions. Nonetheless, further research is required to proof the functionality of this composite material for possible clinical applications.

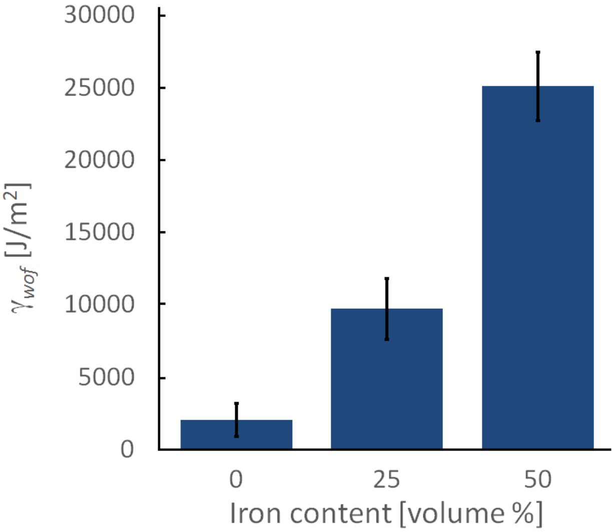

Figure 4. The work of fracture (γ_{wof}) of the composites plotted as function of iron content.

Conclusion

The incorporation of iron in tricalcium phosphate ceramic specimens, consolidated by the spark plasma sintering, considerably increases the toughness, as deduced from the higher energy required to facture these composites. Nonetheless, at the studied chemical compositions, the brittle nature of tricalcium phosphate still dominates the fracture behavior of the composites.

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