Strength and fracture mechanism of iron reinforced tricalcium phosphate cermet fabricated by spark plasma sintering

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Abstract

The present work studies the microstructure and mechanical performance of tricalcium phosphate (TCP) based cermet toughened by iron particles. An additional novelty arises by the employment of spark plasma sintering for fabrication of the cermet. Results showed the alpha to beta phase transformation of TCP, the absence of oxidation of iron particles and no chemical reaction between TCP and iron components during sintering. The values of compressive and tensile strength of TCP/Fe cermet were 3.2 and 2.5 times, respectively, greater than those of monolithic TCP. Fracture analysis revealed the simultaneous action of crack-bridging and crack-deflection microstructural toughening mechanisms under compression. In contrast, under tension the reinforcing mechanism was only crack-bridging, being the reason for smaller increment of strength. Elastic properties of the cermet better matched values reported for bone. Thereby the new TCP/Fe cermet has potential for eventual use as a material for bone fractures fixation under load-bearing conditions.

Keywords: Ceramic-matrix composite; Tricalcium phosphate; Spark plasma sintering; Microstructural toughening; Fractography

1. Introduction

Calcium phosphates (CaP) ceramics provide an attractive basis for the fabrication of implantable devices for orthopaedics, bone tissue engineering, craniofacial and maxillofacial surgeries, and dentistry applications, since they possess excellent biocompatibility, bioactivity and osteoconductivity, promoting stable bone ingrowth and effective bonding at the bone-implant interface [1]. However, they are limited for the application in load bearing components due to their inherent high brittleness and low fracture toughness, which for the monolithic CaP does not exceed $1 \text{ MPam}^{1/2}$ [1] as compared with $2\text{--}7 \text{ MPam}^{1/2}$ for human bone [2]. The incorporation of ductile particles is considered as a promising route for the improvement of the mechanical performance of brittle materials due to the development of different microstructural toughening mechanisms, such as crack-bridging and crack-deflection [3]. The composite materials that exploit the advantages of both ceramic and metallic components are commonly called ‘cermets’. In general, cermets exhibited obvious advantages over monolithic ceramics in terms of improved strength and fracture toughness. In the particular case of CaP ceramics, most of their cermets are composed of hydroxyapatite (HA) matrix, while titanium (Ti) [4-6] or silver (Ag) [7,8] particles were utilized as ductile reinforcements. The thermal degradation of HA matrix during sintering is the most important drawback of resulting HA based cermets, since during sintering Ti reinforcements oxidize forming titanium dioxide (TiO_2) or other oxide products, or react with the HA matrix to form calcium titanate (CaTiO_3) or different Ti-P compounds [9-11]. The above-listed drawbacks can be diminished by the usage of novel sintering techniques, such as spark plasma sintering (SPS) [9], which utilize lower sintering temperatures and shorter processing times than conventional pressure-less sintering routes. The HA/Ti cermets obtained by SPS route show superior mechanical properties and better biocompatibility as compared to those sintered via conventional sintering technology [9]. However, it is worth mentioning that even SPS process did not completely suppress the thermal decomposition of HA [9].

Within the family of CaP, tricalcium phosphate (TCP) is a promising alternative to HA as a material for the cermet matrix. TCP is more stable than HA during sintering and it is as well biocompatible, bioactive and biodegradable ceramic. TCP has two polymorphs, the alpha (α -TCP) and the

beta (β -TCP) phases. Although that the β -TCP is by far mostly used in clinical practice as bone filler material, the α -TCP phase is slightly more soluble [12-14], therefore, α -TCP can allow the fabrication of a new class of biodegradable cermets. This new family of cermets can allow the fabrication of temporal osteosynthetic devices in future. As for the mechanical reinforcement, biodegradable iron (Fe) particles have been recently used together with α -TCP allowing the attachment and spreading of osteoblast cells [15]. Nonetheless, little attention has been paid to the microstructure, mechanical performance and fracture mechanism of these cermets. Therefore, α -TCP/Fe cermets require further and deeper mechanical characterization, in particular if these are to be used in load-bearing applications, such as the fixation of bone fractures.

The subject of the present research is to establish the effect of Fe reinforcements on the microstructural features and correlate this effect with the mechanical performance and fracture mechanisms of the α -TCP/Fe cermet. In particular, the relationship between compression and tension fracture modes are analysed and compared with that of monolithic TCP ceramic, sintered under the same conditions. Sintering of the α -TCP/Fe powder cermet was conducted by the SPS method, which simultaneously applies both temperature and compaction axial-load in order to increase the densification of the material. During the SPS process high electro-magnetic field is induced, which promotes densification of difficult to sinter metastable materials [16-18].

2. Material and methods

2.1. Initial components

The synthesis of initial α -TCP powder was accomplished through the solid-state reaction between calcium carbonate (CaCO_3 ; Lachner 30219-CP0) and calcium hydrogen phosphate (CaHPO_4 ; Merck 102304) powders at a 1:2 molar ratio, according to the following equation:

The precursor powders were preliminary mixed in a rotatory cylinder during 3 h and subsequently aged for 2 h at 1400 °C in alumina crucible in air using a laboratory muffle furnace (Classic Superkanthal furnace 2017). In order to prevent allotropic α -TCP $\rightarrow\beta$ -TCP transformation in the reaction product occurring at ~ 1125 °C [19], the synthesized α -TCP block was subjected to air quenching according to the recommendation given by Carrodeguas *et.al.* [12]. The resulting block (~ 140 g) was subsequently ball-milled in a planetary mill (Fritsch Pulverisette 6) for 20 min at 400 rpm in isopropanol using an agate jar and agate balls (20 balls of 20 mm diameter). The average particle size of the obtained α -TCP powder was in the range of 1-11 μm .

As for the metallic component of the cermet, commercial Fe powder (Fe; Applied Carbon Nano Technologies; particle size $-20+2$ μm) was used in the present study.

2.2. Sample fabrication

The initial powders of synthesized α -TCP and commercial Fe were dry mixed in a rotatory cylinder during 3 h at a volumetric ratio α -TCP:Fe = 3:1. The obtained powder blend was placed in a cylindrical carbon die and consolidated in vacuum using a SPS system (Dr. Sinter 1050, Sumitomo Coal Mining Co., Japan) under the following processing parameters: heating rate of 100 °C/min, sintering temperature of 1000 °C, dwell time of 10 min and uniaxial compact pressure of 35 MPa. The external power source of the SPS system provided a direct electrical current discharge with on–off pulse duration of 12 and 2 ms. To protect the graphite die and plungers and to make the sample release easier after sintering, a 0.13 mm thick graphite foil was used to lay out the die and plungers. After sintering, the samples were cooled down inside the system until 200 °C before being extracted from the die. Two kind of samples were produced, *i.e.* (i) cylinders of 12 mm in diameter and 20 mm in height and (ii) discs of 12 mm in diameter and 5 mm in height. In addition to cermet samples, the samples from pure α -TCP powder were also produced using the same processing parameters and these were used as a reference material in the study.

2.3. Chemical analysis and microstructural characterization

The SPS fabricated samples of monolithic TCP and TCP/Fe cermet were mechanically ground with silicon carbide (SiC) abrasive papers of 320-1200 grit, finely polished with 1 μm diamond paste using a linen disc, cleaned in ethanol ultrasonically and dried in air. The chemical analysis of initial powders and SPS fabricated samples was performed by X-ray diffraction (XRD; Rigaku SmartLab 3kW CF2) by scanning in Bragg-Brentano geometry using Cu K α radiation (50 kV, 50 mA) for the scanning 2θ range between 20-70° at 3 °/min. The crystalline phases were identified from a comparison of the obtained XRD patterns with the international centre for diffraction data (ICDD) powder diffraction files (PDF) (α -TCP: JCPDS 9-348; β -TCP: 9-169; Fe: 6-0696). The microstructure of SPS fabricated samples was characterized with a scanning electron microscope (SEM; TESCAN Lyra3) equipped with an energy dispersive X-ray (EDX) spectroscope (INCA, Oxford Instruments, UK). Prior to microstructural observations, the samples were ground with SiC abrasive papers of 500-2000 grit and finally polished with 1 μm diamond paste. The SEM characterization of cermet microstructure was performed in the backscattered electron (BSE) mode in order to better differentiate composite constituents and other phases due to the difference in atomic numbers. To reveal the grains of monolithic TCP, the samples were subjected to thermal etching, which consisted in thermal exposure of polished samples at 900 °C in air for 10 min followed by fast cooling. The average grain size was measured using the intercept method. In contrast to cermet samples, the samples of monolithic TCP were additionally coated with thin golden layer to prevent the electrical charge during observations and were analysed in the secondary electron (SE) mode. The apparent skeletal density of each material was determined by Helium pycnometry method (Micromeritics AccuPyc II 1340).

2.4. Mechanical characterization

Unconfined compression test (CT) and diametral tensile test (DTT) were performed using a universal testing machine (TIRA test 2850S, TIRA GmbH, Germany) at a constant crosshead speed of 1 mm/min. DTT was performed instead of conventional tensile test to avoid complex gripping and

alignment of brittle samples and is an accepted method to indirectly estimate tensile strength of materials with little or no plastic deformation [20-22]. For each test at least four samples were used and the average values were reported along with standard deviations. The CT samples were cylinders of 12 mm in diameter and 20 mm in height. Compressive strength (CS) was calculated by dividing the load at fracture per the area of the cross section of the sample. The elastic modulus of the cermet under compression was determined from a least-squares fit from the steepest portion of the stress-strain curves.

For DTT analysis, the samples consisted of discs of 12 mm in diameter and 5 mm in height, which were compressed with their axis perpendicular to the applied load. Under this setup, fracture occurs across the specimen diameter and between the points of application of the load. The diametral tensile strength (DTS) of the specimens was calculated according to equation (2) [23]. The unmodified fracture surfaces of the samples after CT and DTT were examined by means of SEM.

$$DTS = F/dh \quad (2)$$

where F is the applied load at fracture, d is the diameter of the sample and h is the sample height.

Hardness was measured under a load of 49.03 N by means of Vickers method using a microhardness tester (DuraScan, Struers, Denmark). Under this load the indentation diagonal was around 70-80 μm , making the hardness values to be representative of the material property. During the indentation test, 16 indents in total were produced on the sample surface and the average hardness values are reported along with standard deviations. After the indentation, the cracks near the edges of indents were analysed using SEM.

3. Results and discussion

3.1. Crystalline composition and microstructure

Figure 1 shows the XRD data of the initial powders and SPS fabricated samples, *i.e.* monolithic TCP and TCP/Fe cermet. The XRD pattern of the as-received Fe powder contained only the peaks of Fe with body centred cubic (BCC) lattice, while the initial TCP powder consisted mostly of α -TCP with some traces of its allotropic β -TCP phase. Despite the air quenching of the α -TCP block, a small quantity of β -TCP phase was formed probably due to cooling rate not fast enough to retain α -TCP in the entire volume of the block or the presence of impurities in raw precursors thus promoting the nucleation of β -TCP [24,25]. In fact, the presence of some β -TCP is typically observed in the final α -TCP powder produced using similar method [24,26]. The crystalline phases presented in the monolithic TCP ceramic were a mixture of both α -TCP and β -TCP. Similarly, the ceramic matrix of TCP/Fe cermet showed the same crystalline composition. In both cases, according to the relative intensities of the diffraction peaks (around 31 degrees), the predominant crystalline phase was β -TCP rather than α -TCP. In other words, the amount of the α -TCP phase was considerably reduced during sintering with respect to the initial α -TCP powder. The evident increase on the β -TCP content in the SPS fabricated samples is a result of the metastability of α -TCP at the sintering temperature, as well as of the high thermal and electrical energy supply to activate diffusive sintering mechanisms, leading to the formation of the more stable β -phase of TCP. Reducing the extent of allotropic transformation requires further optimization of the sintering parameters, for example, increasing the sintering temperature above the phase transition temperature, 1125 °C [19]. This action, however, is out of the scope of the present work. In addition to TCP, the XRD pattern of the cermet presented the BCC peaks of Fe, which acts as the metallic reinforcing component. The absence of Fe oxides or calcium phosphates other than α -TCP or β -TCP shows no evidence of oxidation nor chemical reaction between cermet constituents (TCP and Fe) due to relatively short time of SPS process. This is in contrast to the previous reports about HA/Ti cermets fabricated using conventional sintering [10] or SPS [9,27], where partial decomposition of HA matrix as well as the formation of titanium oxides (TiO_2 , Ti_2O_3 , CaTiO_3) and phosphates ($\text{CaTi}_4(\text{PO}_4)_6$) was commonly observed.

Figure 2 shows the microstructure of the monolithic TCP and representative micrographs from different cross-sections of the fabricated cermet sample, where the white areas correspond to Fe

reinforcing particles, while the dark areas correspond to TCP matrix. Monolithic TCP ceramic exhibited a compact and homogeneous microstructure (Fig. 2a), which consisted of equiaxed grains with a mean grain size of 0.8 μm . The fine grain size was retained primarily due to the low sintering temperature of SPS, at which excessive grain growth was not yet taking place [28]. Regarding the cermet microstructure, Fe particles were found to form large flattened spherical agglomerates with a size up to 150-200 μm (Fig. 2b-d), which was probably caused by Fe powder aggregation during homogenization of the powder blend. As it can be observed from the transverse and longitudinal cross-sections of the SPS fabricated cermet, Fe agglomerates were flattened during sintering in the direction of the applied load according to a scheme shown in Fig. 2e. The formation of such microstructure may have an effect on the anisotropy of the mechanical properties of the cermet.

The relative density of the SPS sintered monolithic TCP (97.5 %) was lower than the relative density of the TCP/Fe cermet (98.2 %). Despite that the TCP matrix of the cermet sample disclose small pores (smaller than 1 μm) in both cross-sections (black dots in Fig. 2 c and d), the addition of Fe particles slightly improves densification of the material during sintering, probably because ductile Fe particles were plastically deformed at high temperature and pressure, closing the voids within the matrix. It is expected that the better densification have a positive influence on the mechanical properties of the ceramic matrix of the cermet, which are highly sensitive to the presence of pores and other microstructural defects. Furthermore, a more detailed microstructural examination (Fig. 3a) revealed that ceramic matrix developed a clear and integrated contact with the Fe reinforcements. The EDX elemental mapping showed no occurrence of any reaction products at the TCP-Fe interface (Fig. 3b-e). In contrast, sharp and well-defined boundaries between elements were observed, which corroborates the observation from XRD about the absence of chemical reactions between components of the cermet. These observations denote good interfacial connection of cermet's constituents required for mechanical stress transmission and consequently matrix reinforcement. Notice that the occurrence of a good interphase contact without the formation of reaction products (oxides of Ca and Fe and Fe phosphates) was possible due the use of SPS

technology at the set temperature (much lower than the melting temperature of both constituents), pressure and sintering time, which avoids solid state reaction between the TCP and Fe components.

3.2. Fracture behaviour under compression

The stress – strain curves during CT for the monolith TCP and the TCP/Fe cermet are shown in Fig. 4. The effect of iron incorporation on the compressive performance is evident, since the CS value attained of the TCP/Fe cermet ($CS = 637.6 \pm 6.1$ MPa) was ~ 3.2 times higher than that of the monolithic TCP (200.4 ± 10.6 MPa). The CS value of monolithic TCP is higher as compared to previously published data for TCP ceramics produced by conventional sintering methods (30-70 MPa) [29,30]. Closer values of CS were reported in the studies that employed non-conventional sintering methods, such as microwave sintering (~ 100 MPa) [31]. While other studies on ion doped TCP reported higher values of CS (315-687 MPa) [32,33]. Such a large scatter of literature data, in comparison to the data obtained in the current study, can be associated with the physicochemical conditions of initial materials, sintering methods and sintering parameters that extremely affect the resulting microstructure, phase composition and porosity. For example, Zhang *et al.* [34] recently demonstrated that the β -TCP $\rightarrow\alpha$ -TCP transformation can induce cracks in the β -TCP ceramic, decreasing its CS from 540 to 130 MPa.

In spite of scarce literature data on TCP matrix cermets, some reports exist on mechanical properties of Ti and Fe based cermets. In general, Ti matrix cermets containing between 10 and 30 % of HA present lower CS (85-250 MPa [35-37]) than the studied TCP/Fe cermet. Even HA matrix cermets with 30 % of Ti particles sintered by SPS present lower CS (390 MPa [9]). On the other hand, Fe matrix cermets containing 5 % of CaP particles present similar CS (~ 700 MPa [38]) than the TCP matrix cermet obtained in the current study, containing only 25 % of Fe particles. Besides, the CS of the new TCP/Fe cermet is superior to that of cortical bone (~ 170 - 190 MPa [39,40]), as well as that of some metallic materials used to fabricate osteosynthetic devices, such as stainless steel and magnesium alloys [41].

In comparison with the monolithic TCP (Young's modulus of 7.5 ± 0.2 GPa), TCP/Fe cermet exhibited higher Young's modulus (28.1 ± 3.1 GPa), because more rigid Fe reinforcement (Young's modulus ~ 211.4 GPa [42]) stiffen the TCP matrix. This effect was achieved because the good interfacial contact between the Fe reinforcing particles and TCP matrix (Fig. 3) allows effective stress transmission from the brittle matrix to the ductile and stiff reinforcement. In particular, the compaction pressure applied during SPS plays a paramount role to improve the interfacial contact, since it allow Fe particles to deform and adapt the shape of the irregular TCP surface. It has to be pointed out that the magnitude of the Young's modulus of the TCP/Fe cermet better fit the elastic properties of cortical bone (Young's modulus ~ 3 -30 GPa [39,40]) than other HA/Ti [5,6] or HA/Ag [8] cermets with Young's modulus in the range of 50 to 80 GPa. Young's modulus closer to the stiffness bone is beneficial to avoid the stress shielding effect due to severe stress concentration on the implant-bone interface [43].

An important observation from CT was that all TCP samples failed preferentially by splitting into pieces along planes parallel to the direction of the applied force. This type of fracture is evidence of stable crack growth initiated by microstructural defects (cracks, pores) subjected to the tensile component of the compressive load [31,44]. The representative micrographs of the fracture surface of the monolithic TCP (Fig. 5) disclose major features of mixed inter- and trans- granular fracture modes. The regions of transgranular fracture, which occupied around 60 – 65 % of the total fracture surface and exhibited flat appearance, alternate with the areas of intergranular fracture of facet appearance. It was earlier shown that for some ceramics intergranular failure suggest larger fracture resistance due to slow stable crack propagation along the grain boundaries, while transgranular failure suggests rapid crack propagation through grains [45]. Thus, substantial contribution of intergranular fracture could be advantageous for toughening of monolithic TCP due to multiple crack-deflections, which is additionally confirmed by the tortuous crack propagation pathway observed after hardness indentations (shown in section 3.4). The reason for that can be biphasic ($\alpha+\beta$)-TCP microstructure of the monolithic TCP ceramic, in which crack-deflection is realized on α - β interfaces, however, to prove this statement more detailed investigations are further required.

The fracture of the TCP/Fe specimens under compression occurred in a shear mode inherent to brittle materials. The major fracture plane crosses the entire specimen, with an angle close to 45° with respect to the loading direction. The micrographs on Fig. 6 display the fractured surface of TCP/Fe cermet failed in compression, where a number of large and small cracks can be observed (Fig. 6a). While TCP matrix of the cermet revealed transgranular fracture (Fig. 6b), the Fe particles were cross-cut in compression-shearing process and partially smeared along the fracture surface, as their fracture surfaces were scraped in a preferential direction exhibiting shear bands and tearing edges (Fig. 6c). Therefore, ductile Fe reinforcements effectively pin the crack surfaces together, provide additional absorption of energy due to plastic deformation before failure, thereby increasing the resistance of the cermet to crack extension (bridging toughening mechanism). Crack-bridging toughening arises due to the mechanical anchorage of the Fe particles within the TCP matrix. Otherwise, in absence of chemical bonding between the reinforcing particles and the matrix, as is the case (Fig. 1 and 3), the particles would detach without plastic deformation, with the consequent vanish of toughening effect. The compaction load applied during sintering promotes the mechanical anchorage of the Fe particles in the matrix, representing a further advantage of SPS in comparison with pressure-less sintering methods.

Besides the crack-bridging, the crack expansion along the TCP-Fe interfaces was observed, that implies the operation of other toughening mechanism, namely crack-deflection. Crack-deflection was previously observed as a major toughening mechanism for some particle-reinforced CaP ceramics, such as HA/Ti cermets [5]. In the present case, the superposition of both crack-bridging and crack-deflection mechanisms acting in TCP/Fe cermet means absorption of more energy in the shear plane and provides higher toughening in comparison with the monolithic TCP, in which case the crack-deflection at grain boundaries is the only acting toughening mechanism.

3.3. Fracture behaviour under tension

The representative stress – diametral strain curves obtained during DTT confirm the strengthening effect of Fe particles on TCP matrix under tension (Fig. 7). The values of DTS for the cermet and the monolithic TCP were 73.2 ± 5.4 MPa and 28.9 ± 15.0 MPa, respectively. The experimental value of DTS for the monolithic TCP was higher than the value reported for TCP ceramics sintered by conventional pressure-less methods (15.9 MPa) [46]. Although the differences in purity of the precursors and α/β ratio should be taken into account when comparing these data, this is a new proof of the superior efficacy of SPS technique over conventional sintering methods [17]. Despite the strengthening effect of Fe particles, the tensile performance of the TCP/Fe cermet was beneath the tensile strength of load-bearing biocompatible metals, but slightly below than the tensile strength of cortical bone (~ 100 - 130 MPa [39,40]). The increase of reinforcement fraction or prevention of the reinforcement aggregation during mixing are two alternatives to improve the cermet tensile performance. However, the latter appears more attractive in order to keep the elastic properties compatible with the bone.

An interesting result derived from this work is the fact that the strengthening effect of Fe reinforcements under tension was not as pronounced as in the case of compression, as the DTS was only 2.5 times higher than that of the monolithic TCP. This could be result of the difference in failure mechanism of Fe reinforcements during CT and DTT. During DTT principal tensile stress is mostly generated perpendicular to the fracture plane, so fracture occurred by rapid propagation of critical defect across the whole sample diameter, producing two symmetrical pieces in the case of the TCP/Fe cermet. In contrast, the monolithic TCP sample crashed into several small pieces, showing less cohesion and higher brittleness than the cermet. Congruently with these observations, the fracture surface of the monolithic TCP exhibited fracture features similar to those observed under compression, in which both inter- and trans- granular fractures can be tell apart (Fig. 8).

The fracture surface of the TCP/Fe cermet after DTT featured a more complex mechanism of fracture (Fig. 9). The TCP matrix showed transgranular brittle fracture with some cracks, while Fe reinforcements encountered with the plane of the crack movement exhibited the features of ductile

microvoid coalescence fracture. This mechanism of fracture is characterized by the presence of conical equiaxed microvoids (so-called ‘dimples’) in the fractured surface and is considered as high energy microscopic fracture mechanism commonly observed for pure Fe under tensile loading [47]. This mechanism involves (1) the initial nucleation of microvoids caused probably by interfacial failure between individual particles or grains within Fe reinforcements, (2) subsequent growth of microvoids and coalescence during plastic flow under tensile stresses and (3) fracture of the whole Fe reinforcement. Such a plastic deformation of Fe particles provides some arresting of the advancing crack tip, thus, developing crack-bridging toughening of the cermet. The operation of the crack-bridging mechanism confirms the good interface interlocking of most of the Fe reinforcements into the TCP matrix. Nonetheless, the crack-deflection toughening mechanism, observed under compression, was not obvious in tension, being probably the reason of the less pronounced strengthening.

3.4. Indentation fracture behaviour

The monolithic TCP showed a hardness value of 4.0 ± 0.2 GPa, which is in the range of 3.6 – 6 GPa reported for dense TCP ceramics [28,48]. Nevertheless, some authors indicated lower hardness (~ 1.7 GPa [29]), which can be affected by the sintering method, resulting porosity and final phase composition. The Vickers’ hardness of the cermet was 2.5 ± 0.3 GPa in the transversal direction and 2.2 ± 0.2 in the longitudinal direction of the samples, which indicates a slight anisotropy of mechanical properties due to preferential flatten orientation of the Fe reinforcements. The cermet’s hardness showed 1.5-fold decrease compared to that of monolithic TCP due to the incorporation of ductile Fe particles, which had hardness of 1.9 GPa. This effect was similar to that formerly observed when ductile metallic particle reinforcements (Ag, Ti) were introduced into hard ceramic matrices (HA, TCP) [5-8,27].

SEM analysis of fracture surfaces showed that monolithic TCP exhibited typical brittle behaviour (Fig. 10a). However, deviation from straight crack propagation confirms the mixed fracture mode taking place with great contribution of intergranular fracture, which is discussed in section 3.2. In spite of its lower hardness, the TCP/Fe cermet exhibited a less brittle behaviour, since crack-bridging occurred at the

position of Fe particles, which prevented the crack development in the Vickers' pyramid corners, and crack-deflections accomplished via interfacial cracking (Fig. 10b). The crack-bridging by the Fe particles was not as pronounced as in case of CT and DTT, or in other words, Fe particles were subjected to plastic deformation without their cross-cutting.

4. Conclusions

Produced TCP/Fe cermet showed substantial improvement in mechanical performance as compared to monolithic TCP. Toughening mechanism of TCP/Fe cermet in both compression and tension involved crack-bridging due to plastic deformation of Fe reinforcements. Under compression, Fe reinforcements failed by cross-cutting in compression-shearing process, while in tension reinforcements failed by ductile microvoid coalescence. Crack-deflection toughening mechanism was observed only under compression, being the reason of the superior strengthening in comparison with tension loading. For the monolithic TCP, crack-deflection at grain boundaries was the only acting toughening mechanism, resulting in simultaneous inter- and trans- granular fracture mode. Results showed that SPS offers advantages over conventionally sintered methods, such as retention of small grain size, improved contact and mechanical interlocking between reinforcements and matrix, prevention of oxidation of reinforcements and avoids the chemical reaction between cermet constituents, although a partial transformation of α -TCP to β -TCP was observed. Despite the high densification achieved for monolithic TCP, its mechanical properties were outside the ranges reported for cortical bone. In contrast, TCP/Fe cermet better matched the mechanical properties of bone, thereby showing a good potential for eventual use as a material for bone fractures fixation under load-bearing conditions.

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6. Disclosures

Authors have no competing interests to declare.

7. References

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Figure captions

Fig. 1. Representative XRD patterns for starting Fe and TCP powders and for SPS fabricated monolithic TCP and TCP/Fe cermet.

Fig. 2. Representative SEM images of the microstructure of the SPS fabricated samples. (a) Microstructure of monolithic TCP ceramic. (b) Microstructure of TCP/Fe cermet tilted at 45°, detail of the (c) transverse and (d) longitudinal sections of the cermet sample. (e) Schematic representation of the TCP/Fe cermet microstructure formation during SPS.

Fig. 3. Microstructure and elemental composition of the of the TCP-Fe interface. (a) Representative BSE image of the interface together with EDX elemental maps for (b) iron, (c) calcium, (d) phosphorous and (e) oxygen.

Fig. 4. Representative stress – strain curves obtained during CT for monolithic TCP (1) and TCP/Fe cermet (2).

Fig. 5. Representative SEM images of the appearance of the fractured surface of monolithic TCP after CT (arrows indicate the position of (1) inter- and (2) trans-granular fracture modes).

Fig. 6. Representative SEM images of the appearance of the fractured surface of TCP/Fe cermet after CT.

Fig. 7. Representative stress – diametrical strain curves obtained during DTT for monolithic TCP (1) and TCP/Fe cermet (2). Diametrical strain was defined as the ratio between the crosshead displacement (U) and the initial diameter of the sample (D).

Fig. 8. Representative SEM images of the appearance of the fractured surface of monolithic TCP after DTT (arrows indicate the position of (1) inter- and (2) transgranular fracture modes).

Fig. 9. Representative SEM images of the appearance of the fractured surface of TCP/Fe cermet after DTT.

Fig. 10. Representative SEM images of the cracks propagated from the corners of the Vickers indentation imprints on (a) monolithic TCP and (b) TCP/Fe cermet. The inserts show the general aspect of the imprints.