The thermal and thermomechanical properties of Ti nanocomposites based hydroxyapatite

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Introduction

Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, HA, is the principal inorganic component of bones and teeth. Synthetic HAP is mainly applied in repair and replacements of hard tissues, presenting excellent biocompatibility. However ceramics HA can be easily decomposed at a temperature depending on the conditions of synthesis, which results in poor sintering characteristics and mechanical properties [1]. The addition of TiH_2 on hydroxyapatite followed by calcination can lead to the formation of a composite with improved mechanical properties without affecting the biocompatibility of the material. Relations between thermal stability and mechanical properties of pure HA and HA+Ti composite ceramics were investigated by thermogravimetric analysis, differential scanning calorimetry and thermomechanical analysis.

Sample preparation

For synthesis of nanocomposites based hydroxyapatite, HA commercial and Ti powder were used. HA commercial (<200 nm, type Aldrich) was calcinated at 900^{0}C for 1 hour in air. The reinforcement is micrometric Ti powder particles (~100 μm, water atomised). The weight ratio between the components is 75% HAP and 25% Ti. The mixture was homogenized for 20 min. in a planetary ball mill, Fritsch – Pulverisette 6, n = 200 rpm, in liquid (ethanol). Then the composite mixture was dried at 200^{0}C in air, and then remixed in the planetary ball mill for 1 min.[2].

Samples characterization

Samples were structural characterized by X-ray diffraction. Fourier transform infrared spectra were measured in the range of 4000–400cm^{-1}, by Nicolet IS 10 spectrophotometer. The specific surface area of the samples were measured by the nitrogen adsorption technique (NOVA 2200e).

Tab. 1. Samples characteristics from XRD and BET

Sample	Composition	Crystallite size (nm)	BET surface area ($m^2\ g^{-1}$)
HA-commercial	$Ca_5(PO4)_3(OH)$ - HA	46	19.192
HA-calcinated	$Ca_5(PO4)_3(OH)$ – HA	145	9.504
HA+Ti	$Ca_5(PO4)_3(OH)$ – HA:75% Ti: 25%	-	9.213

The OH^- libration bands at 630 cm^{-1} are visible on HA calcinated and HA+Ti spectra and the OH^- stretching bands at 3571 cm^{-1} are found on HA commercial and HA calcinated spectra. The characteristic bands due to PO_4^{3-} ions are clearly visible at 568, 601, 962, 1026, 1092 cm^{-1} wave numbers.

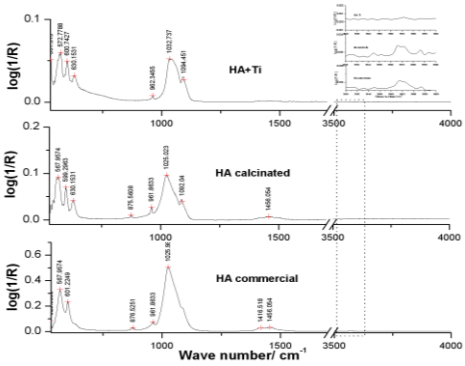

Fig . 1. IR spectra of the samples

Thermal analysis

The thermodynamic stability of the HA and HA-Ti ceramics in the temperature range from 40 to 1400°C was investigated by using a *SETSYS Evolution Setaram* DSC/TG. The experiments were done on powder samples, with a heating rate of 10°C/min, under Ar flow.

The thermomechanical behavior was investigated by using a SETARAM Thermo Mechanical Analyzer (*SETSYS Evolution* TMA). The experiments were done on ceramic samples (pellets form), at a heating rate 5°C/min and under Ar flow.

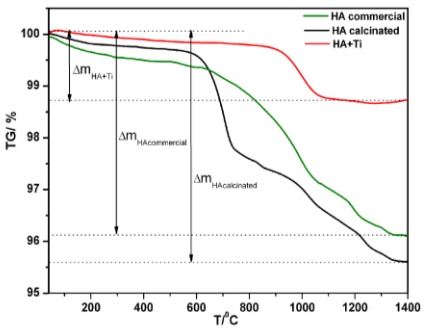

Fig. 2. TG data in the 40 – 1400 ^{0}C temperature range

Sample	Total mass loss (%)
HA commercial	-3,9%
HA calcinated	-4,4%
HA+Ti	-1.3%

Tab. 2. Total mass loss in the 40 – 1400 ^{0}C temperature range

In the temperature range from 40 to 800°C an insignificant mass loss observed on TG curve for HA+Ti sample is in good agreement with the absence of OH^- stretching bands at 3571 cm^{-1} corresponding adsorbed water in the FTIR spectrum.

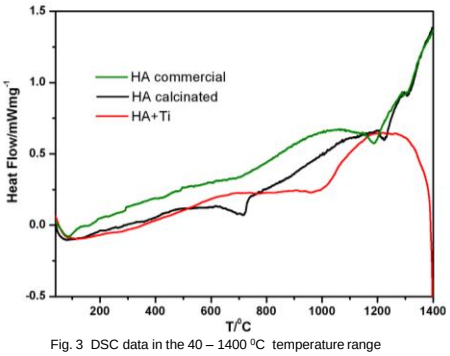

Fig. 3 DSC data in the 40 – 1400 ^{0}C temperature range

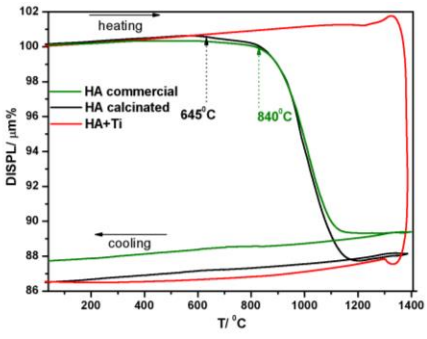

Fig. 4. TMA data in the 40 – 1400 ^{0}C temperature range

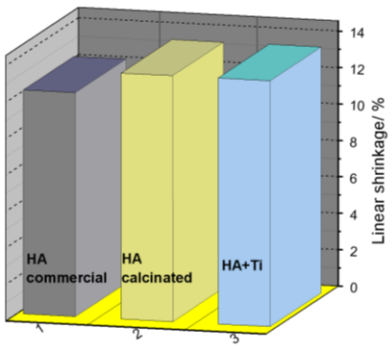

Fig. 5. Linear shrinkage

- The comparison among DSC heating curves of composite HA+Ti and pure HA (commercial and calcinated) indicates that the thermal stability domain of HA+Ti composite is shifted to higher temperatures. The HA decomposition occurs at higher temperature for composite than pure HA (Fig. 3).
- The Ti addition on HA do not affect the linear shrinkage of HA+Ti composite (Fig. 4, 5).

Conclusions

- The influence of Ti addition on dehidroxylation, decomposition and sintering temperature of HA+Ti sample is evidenced.
- HA+Ti Nanocomposite is characterized by a higher thermal stability domain.
- The nanocomposite HA+Ti has improved mechanical properties being an advantage for biomedical applications.

References

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