Review Report on PhD Thesis

Faculty: **Central European Institute of Technology** Academic year: **2019/2020**
Brno University of Technology in Brno

Student: **Mariano Casas Luna**

Doctoral study program: **Advanced Materials and Nanosciences**

Field of study: **Advanced nanotechnologies and microtechnologies**

Supervisor: **doc. Ing. Ladislav Čelko, Ph.D.**

Reviewer**:** **Dr. Konstantinos Georgarakis**

PhD thesis title: Structure and properties of Hydroxyapatite-Magnesium composites produced by the means of current assisted infiltration sintering

Topicality of doctoral thesis:

The thesis deals with the design and development of novel biodegradable composites and their assessment as potential bone-regeneration implant materials. The work incorporates a combination of modern and conventional methods for the fabrication and characterization of structure and properties of interpenetrating composite materials comprised of Mg / Mg alloys and calcium phosphates such as hydroxyapatite, calcium deficient hydroxyapatite or tri-calcium phosphate. The composites were fabricated using an innovative methodology that mainly includes the synthesis of calcium phosphate powders using wet chemistry routes, the preparation of porous ceramic scaffolds by robocasting, and the infiltration of the porous structure with Mg or Mg alloys using the recently developed current assisted metal infiltration technique. Characterization of the produced composites was performed by a variety of methods such as optical and scanning electron microscopy, X-ray diffraction, X-ray microtomography, compression tests, corrosion tests and cytotoxicity tests.

The continuous development of new bio-materials with improved performance in biomedical applications is an important goal relevant to the disciplines of materials science and engineering, biomaterials and biology. The interest in biodegradable implant materials for load bearing orthopaedic applications has been significantly increasing in recent years due to the potential the economic and social impact related with orthopaedic/implant interventions. Thus the topic of the thesis is very interesting, important and up to date.

Meeting the goals set:

The aims and objectives are presented in chapter 3 of the thesis. The work aims to design and manufacture interpenetrating composites using CaP porous preforms infiltrated by Mg and Mg alloys and asses their potential as biodegradable orthopaedic implants. The objectives of the thesis include the chemical synthesis of CaP (hydroxyapatite and tri-calcium phosphate) powders, the fabrication of porous scaffolds by robocasting, the consolidation of the scaffolds and their infiltration by Mg and Mg alloys, the structural characterization of the synthesised composites, and the evaluation of their mechanical behaviour, degradation rates in simulated physiological conditions and cytotoxicity. The goals of the thesis have been met in full.

Problem solving and dissertation results:

The thesis adresses an interesting and imporatnt topic; that of manufacturing biodegradable materials as potential bone regeneration orthopaedic implants by presenting a systematic study on the synthesis of novel interpenetrating Mg/CaP composites and the detailed characterization of their structure and properties.

Porous scaffolds with controlable pore size consisting of stoichiometric HA, CDHA and β-TCP ceramic phases were produced using robocasting. The current-assisted metal infiltration (CAMI) technique was then used to produced composites by infirtating the ceramic scaffolds with molten Mg, Mg-0.2%Ca and Mg-1%Zn alloys (compositions in wt%). The combination of robocasting with CAMI represents an *innovative step for the manufacture of composite degradable biomaterials with designed/archtectured distribution of metal-ceramic phases*. In this study, the process was shown to achieve remarkable infiltartion success of the order 98% of the initial porosity of the scaffolds as a result of both the efficiency of the technique and the chemical afinities of the selected (ceramic/metallic) pairs of materials.

The mechanical behaviour of the syntesized composites was assesed by uniaxial compression tests. The HA based composites exhibited yield strength in the range of 60-70 MPa, mechanical strenth of the order of 120 MPa and plastic deformation before fracture higher than 10%, indicating their potential as low-load-bearing cortical bone substitutions. The Mg/CaP composites exhibited higher corrosion rates than pure Mg and the HA-based composites showed better corrosion resistance compared with their CDHA counterparts. The cytocompatibility evaluation of the synthesized composites showed relatively low affinity with SAOS-2 cells due to the increase in the pH resulting from the relatively fast corrosion. In the proliferation assesment, the bare metals revealed a better cytocompatibility response than their composites. The synthesized interpenetrating Mg/CaP composites exhibit a promising potential as degradable biomaterials; it is suggested that with further development and better control of the microstructure, the degratation rates can be reduced and cytocompatibility can be further enhanced.

Importance for practice or development of the discipline:

The work inroduces a novel processing route for the synthesis of architectured composite structures consisting of CaP porous preforms infiltrated with molten Mg and Mg alloys by

current assisted metal infiltration. The results indicate succesful infiltration reaching 98% of the ceramic preform porosity. The process enables the design of taylored metal ceramic structure and could evolve into an important proceesing procedure in the biomaterials manufacturing discipline. The developed interpenatring Mg/CaP composites show a promissing potential for applications as biodegradeble materials and open a window of opportunities for further developments in the field.

Formal adjustment of the thesis and language level:

The thesis is well organized in chapters: 1) introduction, 2) litterature review, 3) aims, 4) materials and methods, 5) results and discussion, 6) conclusions and suggested future work and includes 168 relevant references. The thesis is well written and the language is clear with only few typos.

Part of the work included in the dissertation has been mainly published in two journal publications, J. Eur Ceram Soc (2019), and Acta Metall Sinica (2017). In both publications Mr Casa-Luna is first author. He has co-authored 12 publications in total (up to date) in the filed indicating a high scientific productivty.

Questions and comments:

-What is the rational for the selection of orthogonal patterns for the scaffold design. Is there an optimal/suggested value (or range) for the ceramic/metallic phase ratio?

-How do thermal expansion coefficients for Mg/Mg alloys compare with the CaP phases? Do (residual) thermal stresses develop during the fabrication of the composites? If so, do they affect the mechanical (and electrochemical) behaviour of the composites?

-How was strain measured in compression tests? How Young's modulus values compare with reported values for similar materials? Why (only) compression tests were conducted for the characterization of the mechanical properties of the produced composites?

-How the performance of the developed composites compare with existing Mg based biomaterials (litterature / commercial) as for example those presented in table 2, page 18?

-"The desire to expand the use of Mg alloys for load bearing applications with controled degradation rate" and the presumption that ceramic reinforcements are able to enhance mechanical properties and corrosion resistance can be considered as part of the motivation for this study. How do you evaluate your findings over this goal and how can you envision overcoming any current limitations?

-What is the significance of the stress shielding effect in low-load-bearing implant applications.

-In fig. 16d, page 53, degradation rates for pure Mg are of the order of 60-70 mm/year, whereas in table 9, page 64, the corrosion rate is about 4 mm/year. How can this difference be explained? In addition, in the chart of fig 16d, there is a spike of corrosion rate to 130 mm/year at 6h; what is the reason for this spike?

Conclusion:

In my opinion, the reviewed thesis fulfill all requirements posed on theses aimed for obtaining PhD degree. The dissertation is of good scientific quality and shows that the researcher is able to conduct original work, carry out analysis and critical evaluation of his research findings and formulate valid arguments and conclussions.

This thesis is ready to be defended orally, in front of respective committee.

Subect to succesful defence, I recomend the award of the PhD to Mr Casas-Luna

In Cranfield, UK , date 02/09/2020

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Dr. Konstantinos Georgarakis