PLASMANT
University of Antwerp

Faculty of Sciences
Department of Chemistry

Prof. Dr. A. Bogaerts

Research Group PLASMANT
Campus Drie Eiken
Universiteitsplein 1
BE-2610 Antwerp-Wilrijk
Belgium

Tel. +32-3.265.23.77
Fax. +32-3.265.23.76
e-mail: annemie.bogaerts@uantwerpen.be
http://www.uantwerpen.be/plasmant

UW KENMERK

ONS KENMERK

DATUM
29-3-2019

BIJLAGE

Report to the PhD thesis of Irina Yu. Grubova

Title: Density functional theory study of interface interactions in hydroxyapatite/rutile composites for biomedical applications
Thesis submitted in fulfillment of the requirements for the degree of Candidate of Physical and Mathematical Sciences (01.04.07 Condensed Matter Physics)
Thesis supervisors: Assoc. Prof. Dr. Roman Surmenev and Prof. Dr. Erik Neyts

This thesis describes DFT studies for the interface interactions in hydroxyapatite/rutile composites for biomedical applications. This is an important research topic, in a growing application field.

Ceramics based on hydroxyapatite (HA) are widely used in many applications (e.g., traumatology, orthopedics, maxillofacial surgery, and dentistry) as coating material for metal implants, and improving the adhesion of metal-ceramic interfaces is an important problem. Atomistic modeling is very useful to elucidate the nature and mechanisms of chemical bonding at the coating/substrate interface, which affect the adhesion strength, with the aim to create materials with specified properties. Although DFT modeling of oxide/oxide and oxide/metal interfaces has been very successful, most modeling studies focus only on a limited range of surface compositions, and only little detailed interface characterization data are available. In this thesis, Ms. Grubova has studied the mutual affinity between HA and Ti surfaces, using DFT implemented in the VASP computer code, in order to gain insight in the nature of the adhesion mechanisms at the interface, and to provide a theoretical direction for experimental correlation.

To reach this goal, Ms. Grubova has (i) constructed theoretical models using periodic slab schemes using supercell cells of amorphous HA (aHA) and TiO2 in rutile configuration (rTiO2), (ii) she calculated the formation energies of bridging and sub-bridging oxygen vacancies, (iii) she studied the effect of atomic structure on the physico-mechanical and electronic properties of the interfaces between aHA surface and various types of rTiO2 slabs, on the interfacial bonding mechanisms, the work of adhesion, the interface energy, the total and partial density of states, and the distribution of the valence charge density, (iv) she calculated the ideal tensile strength for the aHA/aTiO2 interface, to investigate the role of substitution of a P atom by a Si atom in the structure of aHA (aSiHA) in determining the mechanical properties, and (v) she elucidated the atomic and electronic factors responsible for the mechanical stability of HA coatings on the

bx 09/2-104 om 01.04.19

surface of TiO2, in order to suggest a mechanism for enhancing the adhesion and interaction energy at the interface between Ti and the ceramic coating.

The thesis thus contains many interesting and novel aspects, i.e., the theoretical justification of the atomic structure, electronic configuration, mechanical properties and chemical bonding mechanism between Ti and ceramic coating, based on DFT simulations, using the VASP code. This is one of the most efficient and accurate methods for studying electronic properties of low-dimensional systems and nanostructures.

Specifically, Ms. Grubova found that the formation of defects (such as an oxygen vacancy on the surface and in the near-surface layers of the rTiO2(110) surface) is energetically more favorable on the surface of rTiO2(110) than in its subsurface.

In addition, she found that the work of adhesion of aHA on aTiO2 is much higher than on the perfect rTiO2(110) and defective rTiO2 (110) surfaces, and that there are Lewis acid sites at the interface, of which the strength and concentration decreases in the following order: aHA/aTiO2 > aHA/defective rTiO2(110) > aHA/perfect rTiO2(110).

Moreover, she found that replacing the phosphate group by Si anions in the aHA structure leads to a higher adhesion strength, due to a larger number of Ti-O polar covalent bonds across the interface.

Finally she carried out a detailed stress-strain analysis for the interface, and found the presence of a Si dopant in the aHA structure improves the mechanical properties of aHA/aTiO2 interface.

The research findings in this thesis are of great scientific value, and more specifically they provide a better understanding of the microscopic nature of the interatomic interactions and the formation mechanisms of Ti-ceramide coatings. The approach used here to calculate the ideal tensile strength can also be applied to other low-dimensional systems. Moreover, the results also have practical applications, i.e., for the interpretation of specialized mechanical tests of thin coatings formed on metal substrates.

The results of this PhD thesis have been presented at various international conferences and workshops, and have led to 45 scientific papers. I am really impressed by this number, but I cannot imagine that this was all the result of the single thesis. I guess it represents the wider framework of this research, which is not all carried out by Ms. Grubova. Therefore, it would be nice to indicate which papers are specifically the result of the work of Ms. Grubova. Furthermore, it is mentioned that these 45 papers include 3 papers in journals recommended by the Higher Attestation Commission of Russia, but it would be useful to list these paper, and explain what makes these journals of higher value than the journals indexed in Scopus or Web of Science databases. Is it based on their impact factor ?

I am happy to conclude that this PhD thesis by Ms Irina Yu Grubova meets the requirements for the degree of Candidate of Physical and Mathematical Sciences (01.04.07 Condensed Matter Physics).

Best regards and please do not hesitate to contact me if you need further information,

Prof. Dr. Annemie Bogaerts
Head of the research group PLASMANT
Universiteit Antwerpen