THEORETICAL STUDY OF OCTOCALCIUM PHOSPHATE-HYDROXYAPATITE (OCP-HA) INTERFACE MODEL

M. E. Fernández13, J. A. Ascencio1, C. Zorrilla-Cangas2, R. García2 & J. Reyes-Gasga2

1Instituto Nacional de Investigaciones Nucleares, Km. 36.5 Carretera México-Toluca, Ocoyoacac Edo. de México 52045. MEXICO
2Instituto de Física, UNAM, Apartado Postal 20-364, 01000 México D.F., MEXICO
3Posgrado de Ciencia de Materiales, Facultad de Química. Universidad Autónoma del Estado de MéxicoPaseo Colón Esq. Paseo Tollocán Col. Residencial Colón 50140. Toluca, Edo. de Méx. MEXICO

Abstract

Some experimental results indicate that HA and OCP can form an epitaxial interface with a minimum of interfacial energy, producing a smooth HA-OCP interface. The OCP-HA interface has become of great biological interest in the context of mineralized tissue formation. In this work we present the high-resolution transmission electron microscopy (HREM) simulated images obtained from a model of the OCP-HA interface generated after the ideas of Brown et al [1,2,3]. And from this model, based in the idea that the CDL corresponds to an epitaxially growth of HA on the OCP surface, a model for this planar defects also presented. Simulated images were obtained by the multislice method using the atomic positions for Ca, P, O and H as determined by Kay et al. [4] for HA and Brown [2] for OCP respectively. We calculate the model stability by quantum mechanics methods for Brown’s model after relaxation, the atoms had a split of 0.27 Å approximately. In our model the atoms after relaxation kept the same positions.

Key words: Hydroxyapatite, Octacalcium phosphate, Central dark line, Tooth enamel, Image simulations, High resolution transmission electron images.

Resumen

Algunos resultados experimentales indican que la hidroxiapatita y el fosfato ortocálcico pueden formar una interfase epitaxial con un mínimo de energía de intercara, produciendo una interfase HA-OCP suave. Este tipo de interfase es de gran interés biológico en el contexto de la formación de tejidos mineralizados. En este trabajo se presentan imágenes simuladas de microscopía electrónica de alta resolución (HREM) obtenidas de un modelo de interfase OCP-HA generado a partir de las ideas de Brown et al [1,2,3]. Y de este modelo, basado en la idea que la Línea Central (CDL) corresponde a un crecimiento epitaxial de HA sobre una superficie OCP, un nuevo modelo para defectos planares se presenta. Las imágenes simuladas fueron obtenidas por el método de multicapas usando las posiciones atómicas para el Ca, P, O e H, tal como lo determinó Kay et al. [4] para HA y Brown [2] para OCP respectivamente. Se calculó la estabilidad del modelo por métodos de mecánica cuántica para Brown’s model after relaxation, teniendo los átomos una separación de 0,27 A aproximadamente. En nuestro modelo los átomos mantienen la misma posición después de la relajación.

Palabras Clave: Hidroxiapatita, Fosfato Ortocalcico, Línea central oscura, Esmalte Dental, Simulación de Imagenes, Imágenes de Transmisión Electrónica de Alta Resolución.

1. Introduction

Tooth enamel is the most mineralized tissue of human body [1]. The inorganic part is composed mainly by a calcium phosphate named hydroxyapatite (HA) whose chemical formula in its purest state is Ca_{10}(PO_4)_6(OH)_2 [6].

Enamel structure is such that it is composed of many prisms of the order of tenths of microns, which run from the enamel-dentin junction to the enamel surface. These prisms are formed by many elongated crystallites inside the organic matrix. When the enamel crystallites are observed with the transmission electron microscope (TEM), they exhibit a line of 1 to 1.5 nm wide along their centers [7-10]. This line has been named “dark line”, although in its contrast is focus dependent: it appears dark in underfocus, disappears when the image goes through focus, and is white in overfocus [7]. The occurrence of this “line” in the contrast of the enamel crystallites is of particular interest because this zone seems to undergo preferential dissolution during early stages of
the carious process [11,12]. Therefore the knowledge of its structure, properties and chemical composition is very important to understand the role it plays in the enamel structure and, it could be, to combat and prevent the carious process.

Several ideas on the structure of the CDL have been proposed. Specifically that it could be a screw dislocation [13], a twin or grain boundary [7,8], a remnant of a calcified organic material [9] and a localized defect plane of carbonate ions whose unit cell is coherent with the hydroxyapatite unit cell [22]. Dark lines are always localized in the center of the crystallites and seem to be linked to the initial enamel growth mechanisms. Therefore, to find the origin of the dark line, the key is in the analysis of the early stages of enamel mineralization during the amelogenesis.

Cuisinier et al. [14] found the central dark line with a thickness of approximately 1.6 nm in ribbon-like crystals above a minimum thickness of about 8 to 10 nm and running parallel to (10-10) lattice planes. That is, this distance corresponds to two times the (10-10) lattice distance of HA (0.817 nm) or one distance of the (10-10) lattice distance of OCP (1.68 nm).

That the structure of the initially formed thin ribbons is consistent with that of the octacalcium phosphate (Ca$_8$H$_2$(PO$_4$)$_6$$\cdot$5H$_2$O, OCP) has been proposed previously [1,15] but it has not been demonstrated yet. In vitro studies has demonstrated that hydroxyapatite is able to grow epitaxially on the (100) surface of OCP in such a way that the c-axes of HA and OCP parallel to each other [18-20].

In this work we present the high-resolution transmission electron microscopy (HREM) simulated images obtained from a model of the OCP-HA interface generated after the ideas of Brown et al [1,2,3]. And, from this model, the construction of what the CDL structure should be based in the idea that it corresponds to an epitaxially growth of HA on the OCP surface is also presented.

### 2. Simulation procedure

The interface model was obtained by quantum mechanics simulation. Simulated images were obtained by the multislice method (23) using the atomic positions determined by Kay et al [4] for HA and Brown [2] for OCP respectively. Simulated HREM images were obtained with a Silicon Graphics (USA graphic workstation) using the Cerius2 program. The electron microscope parameters simulated corresponded to a Jeol 200. They were: an accelerating voltage of 200 kV, a spherical aberration coefficient of 1.2 mm, a beam divergence half-angle of 0.6 mrad, and a Scherzer resolution of 0.17 nm.

#### 2.1 The OCP-HA interface and the CDL model

Many experimental results [e.g. 14,16,17, 18-20] indicate that HA and OCP can form an epitaxial interface with a minimum of interfacial energy, producing a smooth HA-OCP interface. The growth of HA on OCP is important in the study of the CDL whereas the growth of OCP on HA is important in understanding precipitation processes that occur during remineralization of artificial caries lesions in dental enamel [21].

![Fig. 1. a) Hydroxyapatite unit cell, b) Octocalcium Phosphate unit cell and c) Brown’s interface model](image)

Fig. 1. a) Hydroxyapatite unit cell, b) Octocalcium Phosphate unit cell and c) Brown’s interface model

Structurally speaking, there are some similarities among the unit cells of HA [4] (hexagonal P6$_3$/m, a=9.418 Å, c=6.884 Å and OCP [2] (triclinic P1 or P1, a=19.87 Å, b=9.63 Å, c=6.87 Å, α=90.13°, β=92.13°, γ=108.36°) that is not difficult to imagine how an interface HA-OCP can be built. Therefore, the unit cells of HA and OCP, with the atomic positions for Ca, P, O and H as determined by Kay et al. [4] and Brown [2] respectively, were generated (Figure 1).

In the present work we proposed a new interface, this is formed by half unit cell of HA, which corresponds to (200) plane in figure 1a (the plane AA) and will be glue with the OCP unit cell through the (100) plane (BB in figure 1b). In figure 1c, the interface was generated by glue the planes indicated along the c axis.

In the present work we proposed a new interface, this is formed by half unit cell of HA, which corresponds to (200) plane and one cell of OCP in the (100) plane. In such a way that $c_{\text{HA}}$ is parallel to $c_{\text{OCP}}$ and $b_{\text{HA}}$ is parallel to $b_{\text{OCP}}$, this is [00-1]$_{\text{HA}}$/[001]$_{\text{OCP}}$ and [100]$_{\text{HA}}$/[100]$_{\text{OCP}}$. Figure 2c shows this interface along the [0001] axis.

Both interface were calculated by Density Functional Theory. This process works in such a way that the geometry of the system is optimized, the energy of system is evaluated and the density of the systems is solutioned. We can determinated the stability of the system and if the atoms around the interface have the same environment in both sides of the interface.
The total energy for Brown’s model interface was -227886.15 eV, while for our interface model was -239776.69 eV. As can it be seen the minimum energy is for our interface. Figure 3 shows the charge density a) HA unit cell (200) plane in [001], b) OCP unit cell (100) in [001] and c) interface plane of the interface. For the Brown’s model we can observed in this figure that the environment at the atoms around the interface in not exactly the same as is the HA and OCP units cells.

Figure 4 shows the charge density for our interface model a) HA unit cell (200) plane in [00-1], b) OCP unit cell (100) in [001] and c) interface plane of the interface. Check here that the environment in the interface almost the same as in the HA and OCP units cells.

We analized our interface after relaxed, mainly the distances P-O, Ca-O, and O-H. The P-O length bond reported in literature is 1.63 Å [24], however in the HA unit cell this distance is variable from 1.52 Å to 1.54 Å; and for OCP unit cell it is in the range from 1.51 Å until 1.57 Å. The interface model after relaxation show small variations at P-O distances which are in the range from 1.47 Å to 1.54 Å. The distances for Ca-O and O-H reported in literature[24] are 2.25 Å, 0.96 Å respectively, however in the HA unit cell this distance is 2.34 Å for Ca-O and 0.94 Å for O-H, the distances after relaxation don’t change considerably these are 2.33 Å and 0.93 Å for Ca-O and OH respectively.

Figure 5. Shows high resolution electron microscopy image simulated focal serie of the interface model along the [011] axis that was obtained by SimuLaTEM program. The interface model was used 27 units cell for HA and 24 units cell for OCP, the calculations were done with

Fig. 2. Hydroxyapatite unit cell, b) Octocalcium Phosphate unit cell and c) Interface model proposed

Fig. 3 Charge density a) HA Unit cell (200) plane, b) OCP unit cell (100) plane and c) interface plane of the interface.

Fig. 4. Charge density a) HA Unit cell (200) plane, b) OCP unit cell (100) plane and c) interface plane of the interface from our model.

Fig. 5. Interface HA-OCP HRTEM Simulated Images Focal Serie [011] with different thickness.
The CDL model was made using two supercells of HA formed with 4 unit cell along a axis, one unit cell along c axis and 27 units cells along b axis (4x27x1) of HA and one supercell of OCP (2x24x1) units cells. That this way the CDL model is formed by one supercell of OCP which is between two supercells of HA. Figure 8 shows high resolution electron microscopy image simulated of the CDL model along the [011] axis (Figure 8a) and [001] axis (Figure 8b).

3. Discussion

In order to reproduce an epitaxial growth and highly coherent interface between HA and OCP, as the experimental results indicate, the interface was formed by half unit cell of HA and one cell of OCP in such a way that [0001]_{HA}//[001]_{OCP} and [10-10]_{HA}//[010]_{OCP}. Everything indicates that it is unnecessary use of one half of the HA unit cell and not a complete one to build the interface. Moreover, it was found the planes (0001) of HA and (001) of OCP are not coplanar. The atoms around of the interface don’t have the same environment in both sides of the interface this is showed in Figure 2, where a) is HA charge density slice in (200) plane, b) is OCP charge density slice in (100) plane and c) interface charge density slice.

However our interface model the atoms around the interface must fill the same environment in both sides of the interface this is showed in Figure 4 where a) HA charge density slice in (200) plane, b) OCP charge density slice in (100) plane and c) interface charge density slice, we can see the same charge density distribution.

The distances between main atoms of P, Ca, O and H have an average difference 0.006 Å after relaxation, however the charge density distribution preset the same environment atoms for HA, OCP and interface.

The image simulation of HA-OCP interface model reproduce experimental contrast as indicate the Figure 6 where we can see that the experimental and simulation image are very similar.

Experimental evidence indicate that human dentine crystal formation involving conversion of octacalcium phosphate to hydroxyapatite, its is known as CDL [26], according with the simulations results is possible the existence the HA-OCP interface and as consequence the existence of CDL.

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References