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Laser assisted mineralization of dental hard tissues

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Abstract: Here we present a platform technology for the direct sintering of calcium phosphates on dental hard tissues using femtosecond lasers. Different parameters are investigated in order to obtain the optimum layers. (31 words- max 35)

1. Introduction

Dental enamel is the outermost hard tissue, protecting the softer dentine structure from oral challenges. Enamel has a unique microstructure and extraordinary mechanical properties as it is the hardest tissue of human body. In contrast with other hard tissues, such as the bone and dentine, enamel is an acellular and thus lacks the ability to heal itself. The lack of regenerative potential leads to perpetuation of acid erosion of enamel in oral acid environment and as this erosive wear progresses by exposing dentine possible complications are pain, pulpal inflammation, necrosis, and periapical pathology. In these cases, the intervention of clinicians is essential but an effective, long term solution for the restoration of enamel is not yet available.

Guided by the principles of personalised medicine and based on the fundamentals of Selective Laser Sintering (SLS), we developed a procedure where **direct laser sintering**, **densification** and **bonding** of a layer of ceramic biomaterial on the surface of eroded enamel can be achieved. Such a technology not only can be used for treating hypersensitivity but could also find a unique space of applications in restorative dentistry and orthopaedics for the rabid restoration of hard tissues. Conventional sintering and densification of ceramics (e.g. calcium phosphate materials) takes place at a temperature range between 1000 and 1500 ˚C [1]. Achieving the same result on the surface of a hard tissue without inducing any thermal damage, is a challenging and high-risk task. To be successful, numerous variables need to be taken into consideration; i) type of the laser; ii) irradiation parameters; iii) the properties of the biomaterial that will be attached on the hard tissue; iv) the properties of the initial coating.

The aim of this work is to discuss the different variables that affect the sintering and attachment of ceramics on hard tissues (e.g. type of laser, average power, type of biomaterials) and to demonstrate the attachment of a layer of calcium phosphate on the surface of dental enamel with **minimal thermal damage for the tissue**. The sintered layers are characterised for their chemical, structural and mechanical properties (XRD, SEM, nano-indentation) and the induced thermal damage to the hard tissues is evaluated.

2. Methodology

All the calcium phosphate minerals used in this work (i.e. brushite, hydroxyapatite and fluorapatite) have been synthesised through wet precipitation method at temperature of 37 ˚C and pH=5.4 for brushite and pH=8 for hydroxyapatite and fluorapatite [2], [3]. To enhance the laser-biomaterials interaction, we doped the minerals with 10% Fe^{2+}/Fe^{3+}. For laser irradiation experiments bovine enamel blocks have been coated with a mixture of chitosan solution and the corresponding mineral powder. Three different lasers have been utilised i.e. a CW laser emitting at 976 nm (System A: LIMO32), a femtosecond pulsed laser with repetition rate of 1 kHz and emission at 800 nm (System B: Ti:Shaphire, LIBRA) and an ultrafast femtosecond pulsed laser with repetition rate of 1 GHz and emission at 1040 nm (System C).

3. Results and discussion

3.1 Type of laser: It was proved that with the CW system we can partially melt the coating on the surface of enamel (average power of 0.5 W) while, at high average power (>0.8 W) we observed cracking and burning of the hard tissue. With System B, ablation was the dominant mechanism of laser-matter interaction and consequently there wasn't any attachment of new material on the surface of our samples. The best results have been obtained with System C since we managed to form compact layers of fluorapatite and hydroxyapatite on the surface of dental enamel (**Figure 1**). The thickness of the new layers is between 20 and 30 μm and after nano-indentation the mechanical properties found to be very close to that of dental enamel and natural bone (**Table 1).**

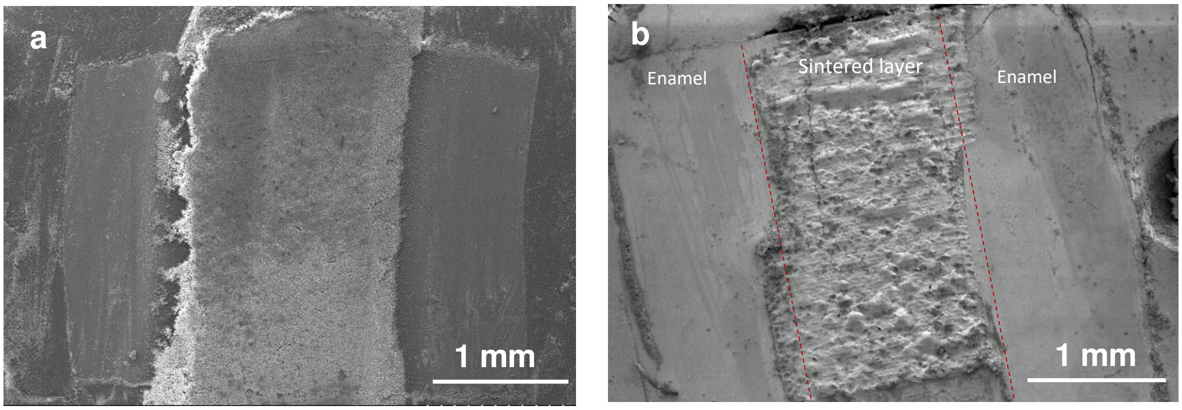

Figure 1: Coated dental enamel before and after sintering; a) pre-sintered dental sample coated with a mixture of chitosan and fluorapatite crystals; b) sintered fluorapatite layer after irradiation with system C (0.6 s exposure time and 0.4 W average power).

3.2 Average power: After we identified the appropriate laser (system C), our efforts were focused on optimising the laser energy. Starting from 0.1 W we conducted experiments by increasing the average power by a step of 0.05 W. We observed that minimum power where sintering is taking place is 0.2 W. Although there are clear alterations on the surface of the coating, the delivered energy is not sufficient for bonding the mineral to the enamel. As it is depicted in **Figure 2a** the coating can be removed after sintering. Based on our experiments, bonding can be achieved for average power higher than 0.45 W (e.g. **Figure 1b** is for average power 0.5 W). In this case there is strong attachment of our mineral with the enamel and after checking the cross sections of the samples we verified that the thermal damage is restricted in a zone of **5 μm** below the enamel-coating interface. By increasing the average power of the laser, we get smoother layers with better mechanical properties (i.e. hardness) however, there is considerable thermal damage to the enamel. For example, for average power of 0.9 W (**Figure 2b**) we observe extensive cracking on the surface of the enamel and close to the interface with the sintered layer.

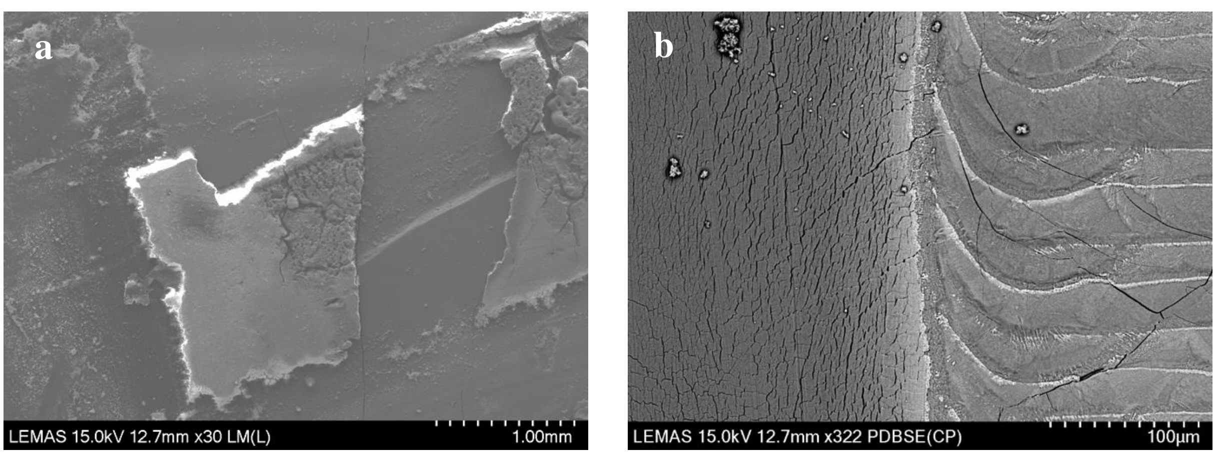

Figure 2: Sintered layers for different average power of the laser (system C, coating of 10% Fe-doped fluorapatite); a) average power of 0.2 W; b) average power of 0.9 W.

3.3 Type of mineral: From the beginning of our research our efforts were focused on three different apatites i.e. brushite ($CaHPO_4 \cdot 2H_2O$), fluorapatite ($Ca_5(PO_4)_3F$) and hydroxyapatite ($Ca_5(PO_4)_3(OH)$). Upon heating, brushite losses two molecules of water and is transformed into monetite. Further heating results in the transformation to γ- and β- pyrophosphate. Similar transformations were also observed during the laser irradiation of the brushite coatings. Because of the radical change in crystal structure, there was shrinkage of the sintered layers and formation of microporosity, leaving exposed the surface of the underlying enamel. On the other hand, both hydroxyapatite and fluorapatite, resulted in dense layers. Also, in both cases after sintering we identified the formation of tricalcium phosphate.

3.4 Mechanical properties: The most promising results were obtained for fluorapatite as the coating mineral and for average power of 0.5 W. For these parameters, the thickness of the new layer is between 20 and 30 μm and the mechanical propertied are very close to that of dental enamel and natural bone (**Table 1**).

Table 1: Mechanical properties of natural enamel and the sintered layer as measured by nano-indentation.

Material	Hardness, GPa	Young's modulus, GPa	Poisson's ratio
Enamel	3.10±0.12	38.67±1.9	0.25
Sintered layer	1.10±0.16	20.50±1.2	0.27
Human bone	0.58-0.80	17.0-20.0	0.30

4. Conclusions

This work successfully demonstrates the concept of direct laser sintering of calcium phosphates on dental hard tissues with the use of ultrafast femtosecond lasers. Although more research is required for the translation into clinic this is the first step for the rabid restoration of hard tissues.

3. References

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