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Laser assisted restorative mineralization of dental enamel

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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.

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 acellular and, therefore, 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 the 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 rapid 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 for the: i) type of the laser, ii) irradiation parameters, iii) properties of the biomaterial that will be attached on the hard tissue, and 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 the chemical, structural and mechanical properties (XRD, SEM, nano-indentation) and the induced thermal damage to the hard tissues is evaluated.

2. Methodology

The calcium phosphate minerals used in this work (i.e. brushite, hydroxyapatite and fluorapatite) were synthesized using 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, the bovine enamel blocks were coated with a mixture of chitosan solution and the corresponding mineral powder. Four different lasers were utilised i.e. a CW laser emitting at 976 nm (System A: LIMO32), a femtosecond (fs) pulsed laser with repetition rate of 1 kHz and emission at 800 nm (System B: Ti:Shaphire, LIBRA), an ultrafast fs pulsed laser with repetition rate of 1 GHz and emission at 1040 nm (System C) and a 1020 nm fs fibre laser with 100 MHz repetition rate (System D).

3. Results and discussion

3.1 Type of laser: It was found that with a CW 976 nm laser, it was only possible to partially melt the mineral coating on the surface of enamel (average power of 0.5 W) while, at high average power (>0.8 W) we observed cracking and charring of the hard tissue. When using the Laser System B, ablation was the dominant mechanism of laser-matter interaction and consequently, the mineral was not found to adhere onto the eroded enamel surface. The best restorative results on bovine enamel slabs were found with the near-IR laser systems [C] and [D], each operating at high repetition rate in 1 GHz and 100 MHz range, respectively. The control of high repetition rates offers the optimal power for achieving the required sintering and adherence of new layer with the natural enamel underneath. We formed compact layers of fluorapatite and hydroxyapatite on the surface of dental enamel (**Figure 1**).

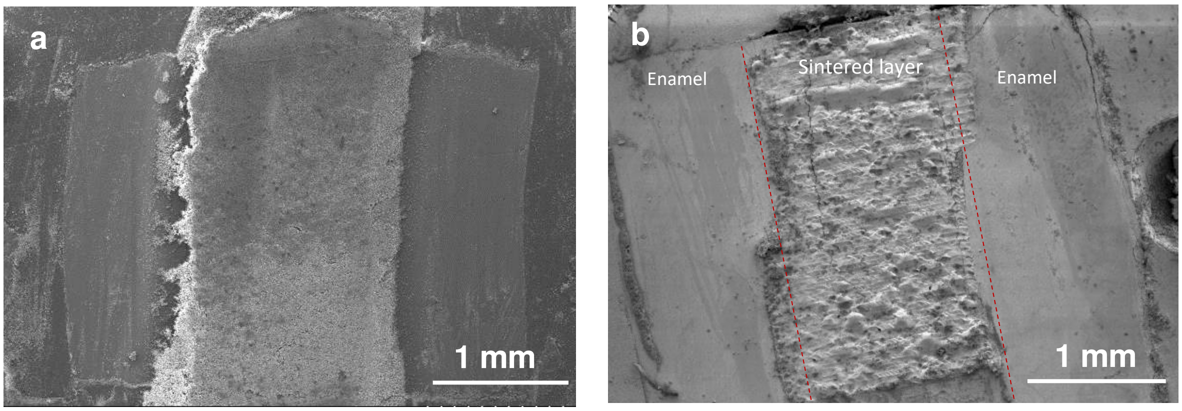

Figure 1: Coated dental enamel before and after sintering; a) pre-sintered dental sample coated with a mixture of chitosan and fluorapatite crystals; b) sintered fluorapatite layer after irradiation with system C (0.6 s exposure time and 0.4 W average power).

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.

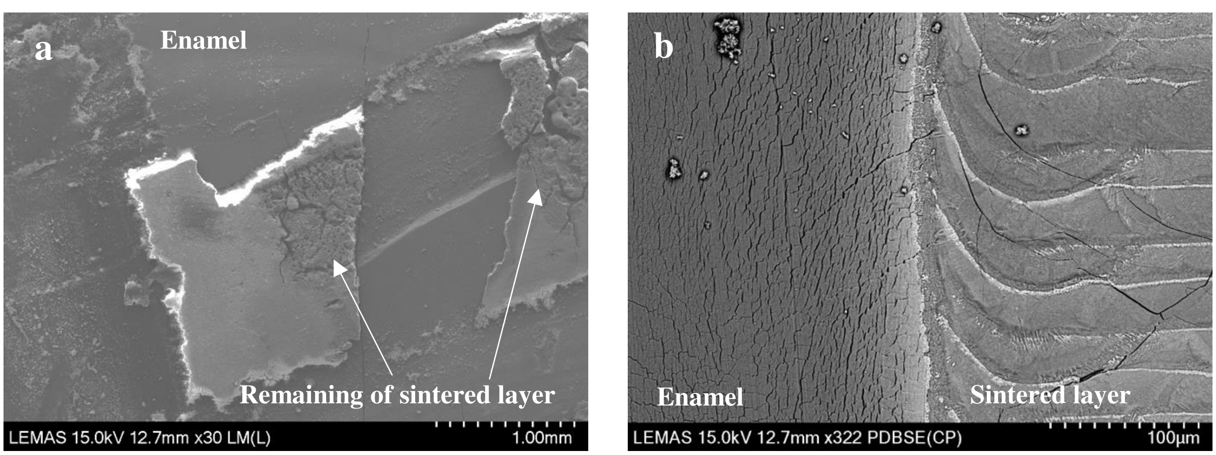

Figure 2: Sintered layers for different average power of the near-IR fs-pulsed laser (system C, coating of 10% Fe-doped fluorapatite); a) average power of 0.2 W. Although we can recognise superficial sintering of the coating this is not bonded to the enamel; b) average power of 0.9 W.

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 properties 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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