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Modification of Hydroxyapatite Crystal Using CO_2 Laser
- The Preliminary Study for FEL Application in Biological Field

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Abstract: To remineralize the dental surface, Laser application was concerned in this study. The purpose of this experiment was concentrating to investigate crystal structure change of hydroxyapatite before and after laser irradiation. The wavelength of incident laser beam is matching the characteristic absorption peak of HAp which ranging around 10 μ m. As a preliminary study for Free Electron Laser (FEL) application in biological field, the results we have got with the 10.6 μ m irradiation indicated that the FEL's capability of precisely deliver energy over a wide band of infrared makes it an attractive tool for further ameliorating of hydroxyapatite crystallization.

Key words: Hydroxyapatite, Remineralization, Dental enamel, X-ray Diffraction.

1. Introduction

The first application of laser technology to dentistry was for the removal of caries infected material and preparation of cavities[1]. However, ever since reports of laser application on improvement of dental surface were emerged, much attention has been focused on the laser's potential to enhance enamel's hardness and resistance to acid[2] [3] [4].

Although many attempts have been made to alter the tooth structure in order to increase its resistance to dental caries, little understanding on the physicochemical mechanisms involved has been achieved [5]. This research has pursued the photochemical phenomenon occurred during laser irradiation on artificial and biological HAp. In order to find a creative method to remineralize the demineralized enamel or the exposed coronal of dentine, the authors developed a novel procedure during laser irradiation [6].

Free electron laser (FEL) application is also intended primarily to realize the same purpose. The micro-pulse structure and duration of FEL laser was expected to be suitable to modify dental surface efficiently [7] [8].

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In this study, slice samples of sound molar and artificial HAp pellet were irradiated with 10.6 μ m CO_2 laser separately. Various laser parameter and chemical conditions were applied in the experiment. Three series of samples covered with saturation calcium ion solution ($Ca(OH)_2$ and $CaHPO_4$) and their combination were compared after irradiation. To investigate the micro-crystal morphology of the samples, X-ray Diffraction (XRD) pattern were surveyed. The comparison of XRD result shows that the chemical coating affected the irradiation process evidently.

2. Experimental Procedure

2.1 The parameter of incident laser

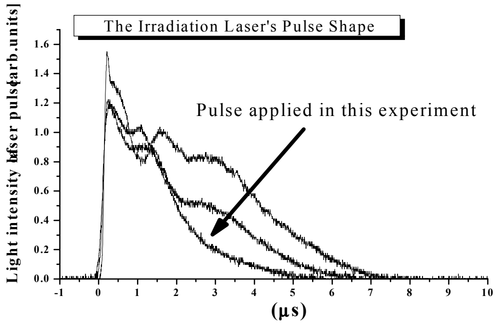

Fig. 1 The flexible pulse of TEA-CO_2 laser

Irradiation was performed with 10.6 μm wavelength TEA-CO_2 laser. It gives out pulses around 1 μs (FWHM) at a repetition rate of 0.2Hz. The mean output energy was modified from 86mJ to 622mJ. Laser beam was focused onto the target surface perpendicularly to attain energy density varying from 2J/cm^2 to 9J/cm^2. The average power was ranging from 18mW to 130mW. While as the power density from 4.89W/cm^2 to 35.23W/cm^2.

Figure.2 shows the pulse shape that we can modify by changing gas ratio in the laser chamber. The pulse, which has the shortest FWHM, as it is shown in Fig.1 was used as the incident beam in this experiment.

The specific experimental conditions concerned in this experiment are following:

(1) XRD survey of original and CO_2 laser irradiated artificial HAp.
(2) XRD survey of dentine and enamel before and after CO_2 laser irradiation.
(3) XRD survey of enamel after CO_2 laser irradiation (covered with saturation chemical solution film).

2.2 The XRD analysis

The X-ray diffraction of the profile breadth and relative intensity data were collected from the samples on a X-ray diffractometer using CuKα radiation (RINT 1100, Rigaku, Japan).

The divergence slit was 1° and the receiving slit was 0.3mm. The scan range for relative intensities was from 20° to 70° (2θ) ; the scan rate was 4° (2θ/min).

3. Results and Discussion

Compared with artificial HAp sample, the (213) (202) reflections intensity of dentine was not so intense. After irradiation with $CaHPO_4$ solution film, the reflection (202) appeared. And the relative intensity peaks of artificial HAp pellet sample, (002) (202) (222) was modified. Most of the characteristic peaks of HAp were decreased.

Through the result we can suppose that HAp may be decomposed due to the thermal effect of laser irradiation [9], while as the product of decomposed HAp also exists in the dentine and enamel as amorphous calcium phosphate phase. The general reaction of HAp infused with chemical solution under the photo-thermal effect condition is considered as following.

$$3Ca_3(PO_4)_2+Ca(OH)_2 \rightarrow Ca_{10}(PO_4)_6(OH)_2+2H_2O+4CO_2 \quad (1)$$

Due to the thermal effect during photo ablation process, the temperature of the interaction surface should raise instantaneously. HAp may be decomposed through the reaction as formula (2).

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 3Ca_3(PO_4)_2+CaO+H_2O \quad (2)$$

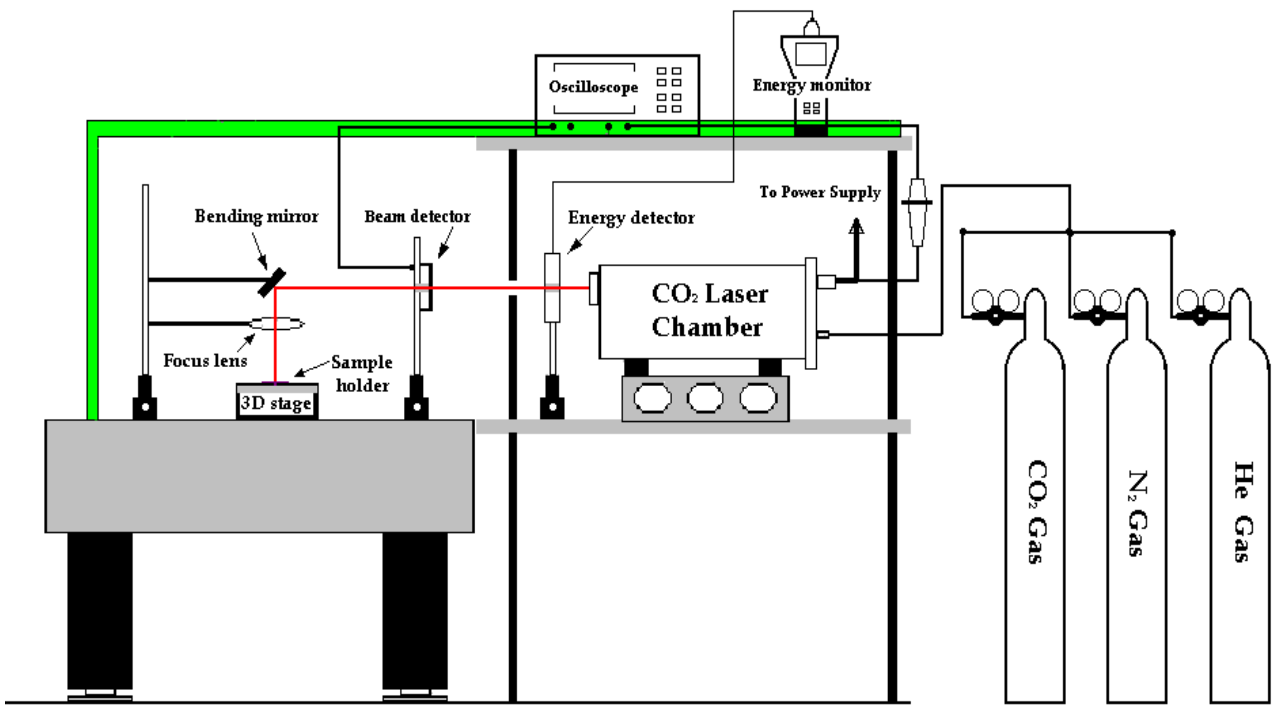

Fig. 2 The scheme of irradiation experiment

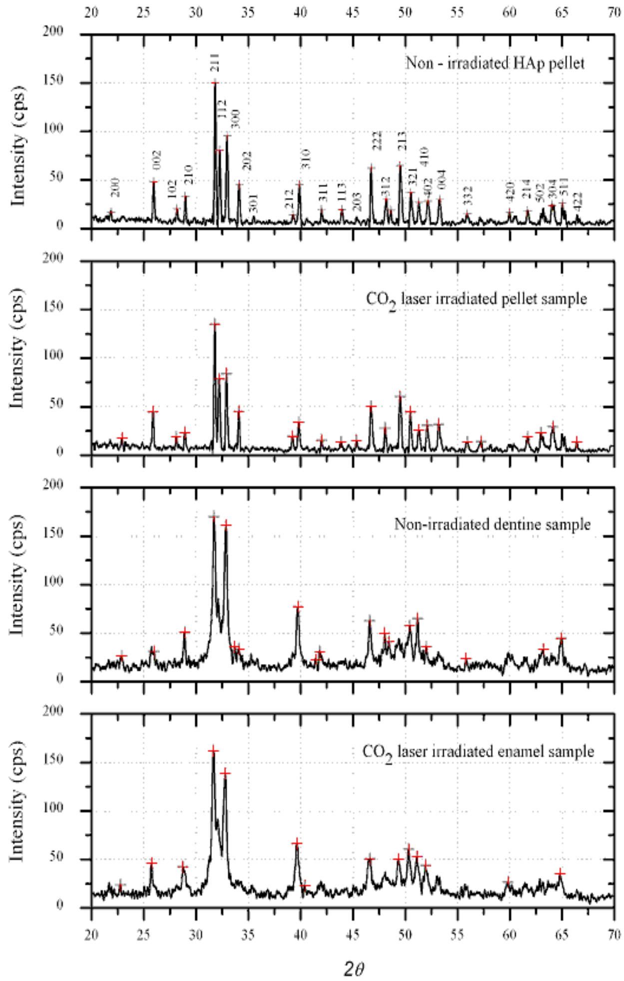

Fig.2 Comparison of CO_2 laser irradiation on artificial HAp and dentine sample

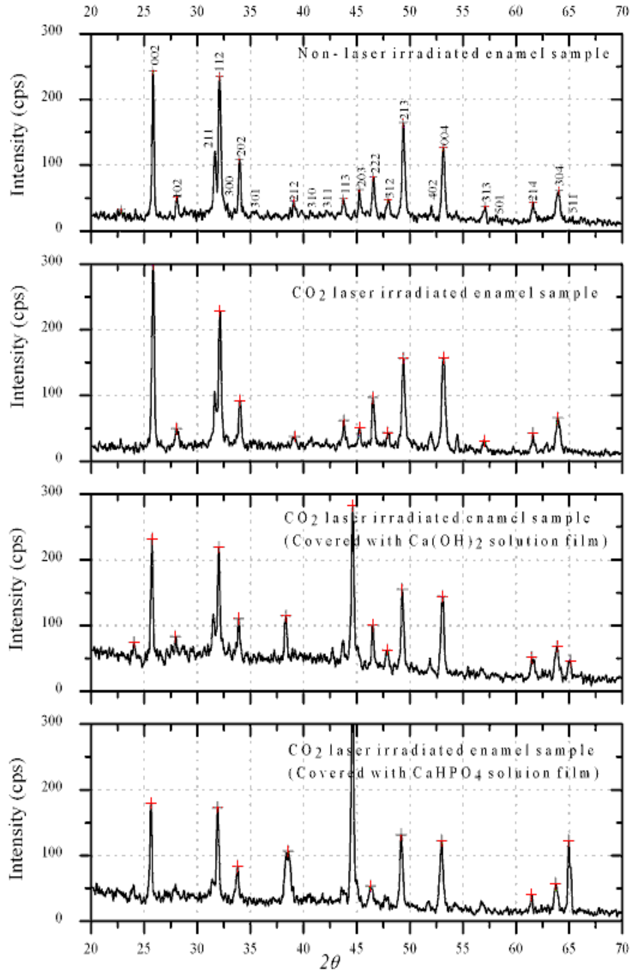

Fig.3 Comparison of CO_2 laser irradiation on dentine sample, with and without chemical solution

And CaO is easy to react with water, and then produce tricalcium phosphate and heat.

The potential reaction under the irradiation with $Ca(OH)_2$ and $CaHPO_4$ mixed saturation solution film was considered as following reaction:

$$4Ca(OH)_2+6CaHPO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2+6H_2O \quad (3)$$

As $CaHPO_4$ is easy to react with $Ca(OH)_2$ to produce various calcium phosphate formations. At the same time, the reaction will release amount of heat. This may delay the heat transmittal and decrease the thermal threshold of hard tissue during irradiation. The apparent amorphous regions of XRD pattern were considered to be connecting with this mechanism.

4. Conclusion

After CO_2 laser irradiation, the (002) reflection was increased significantly. It indicates the crystal growth in c-axis. On the other hand the (222) reflection was reduced both in HAp pellet case and dentine case. It was considered relating to the thermal effect during high-energy irradiation.

The laser energy density performs superior role during the irradiation process compared with the total fluence of energy while fluence is also a very important parameter to control the reaction.

For the $Ca(OH)_2$ solution coated case, obvious remineral process occurred via the hydroxyl contained in the solution enhanced the pH value of the sample surface. The environment should have been modified more appropriate for calcium ion to bond with apatite matrix.

After the irradiation with $Ca(OH)_2$; $CaHPO_4$ combined saturation solution coating, most of the reflection peaks increased except for (310). And the pattern of tricalcium phosphate emerged. It should be the product of chemical reaction during ablation. We believe that the presence of $CaHPO_4$ and $Ca(OH)_2$ could be a trace of the original reaction used to produce HAp.

Acknowledgments

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