MODIFICATION OF HYDROXYAPATITE CRYSTAL USING IR LASER

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Abstract

To remineralize the dental surface, infrared (IR) laser was applied. The purpose of this experiment was concentrating to investigate crystal structure change of hydroxyapatite (HAp) before and after laser irradiation. The wavelength of incident laser beam is matching the characteristic absorption peak of HAp which ranging around 10μm. As a preliminary study for Free Electron Laser (FEL) application in biological field, the results we have got with the 10μm 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.

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 efficiency [7], [8].

In this study, slice samples of sound molar and artificial HAp pellet were irradiated with 10.6 μm CO_2 laser separately. Various laser parameter and chemical condition were applied in the experiment. There 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 effected the irradiation process evidently.

EXPERIMENTAL PROCEDURE

Experimental layout

Experimental setup shows Figure 1. A transversely excited atmospheric pressure (TEA) CO2 laser, which works at pulse width τ=1μs (FWHM) and wave length λ=10.6μm was employed. This equipment permits the selection of the pulse energy from 60mJ to 500mJ, and of the repetition rare from 0.2Hz to 1Hz. The laser output beam was focused by a plano-nonvex ZnSe lens on the front side of the samples to spot sizes of the order of 10^{-2} cm^2, which corresponding energy density of 9J/cm^2. Laser pulse energy was measured with an energy meter (Gentec, Model ED-500L) prior to and after tissue irradiation and pulse-to-pulse stability of the CO2 laser was 23%. Some experiments show that the fluence threshold at this parameter are 0.3J/cm^2 and 0.6J/cm^2 for dentin and enamel respectively. For our experiment, the ablation threshold was estimated approximately 1J/cm^2. The teeth samples used in this experiment are obtained from the Department of Oral and Maxillofacial Surgery, Faculty of Medicine, Saga University. Extracted sound human molars were conserved in a physiologic serum to avoid cracking due to dryness and then embedded into polyester resin and cut into slices less than 1mm thick by a diamond saw microtome. After sliding, the slide discs were polished with a series of water-lubricated SiC papers up to 5000. Thus, enamel and dentine region were prepared flat and accessible to laser treatment.

Additionally, artificial HAp pellet was chosen as the target material for comparison. The Ca/P molar ratio value of the HAp pellet (PANTAX, Japan) was 1.67, which confirms the stoichiometric value. The HAp pellet samples present a high crystallinity as it was demonstrated by X-ray diffraction.

In the irradiation experiments, the specimen was mounted on a motorized x-y-z translation stage and positioned perpendicular to the direction of laser incidence. All experiments have been performed in air. The incidence area was constantly changed to avoid carbonization.

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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 covered with saturated chemical solution film after CO_2 laser irradiation.

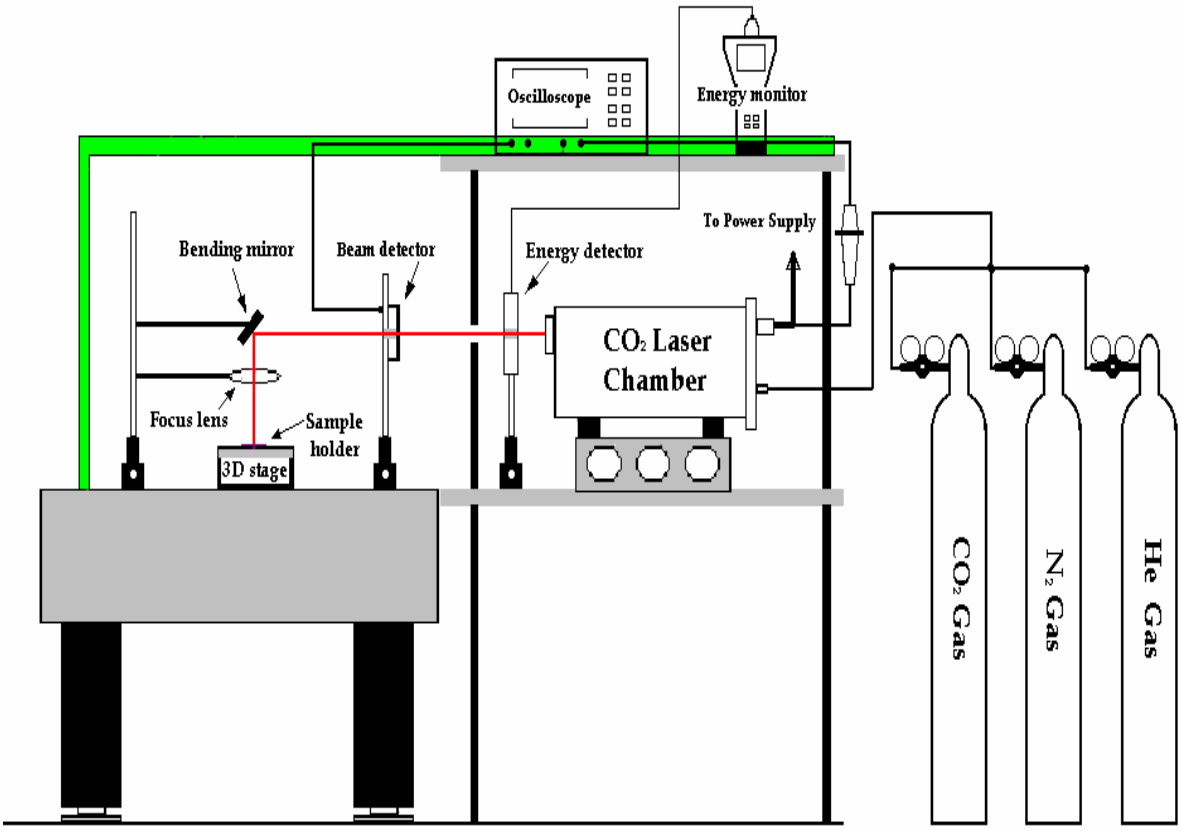

Figure 1: The scheme of irradiation experiment

The XRD analysis

The X-ray diffraction of the profile breadth and relative intensity date were collected from the samples on X-ray diffractomerter using Cu(Kα) radiation (RINT1100, Rigaku, Japan). The divergence slit was 1° and the receiving slit was 0.3mm. The scan range for relative intensities was from 20º to 70º (2θ), and scan rate was 4º (2θ/min)

RESULT AND DISCUSSION

Compared with artificial HAp sample shown in Figure 2, the (213) and (202) reflection intensity of dentine was not so intense. After irradiation with $CaHPO_4$ solution film shown in Figure 3, the reflection (202) appeared. And ten 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 [8], 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).

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

And CaO is easy to react with water, and the 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.

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

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 patter were considered to be connecting with this mechanism.

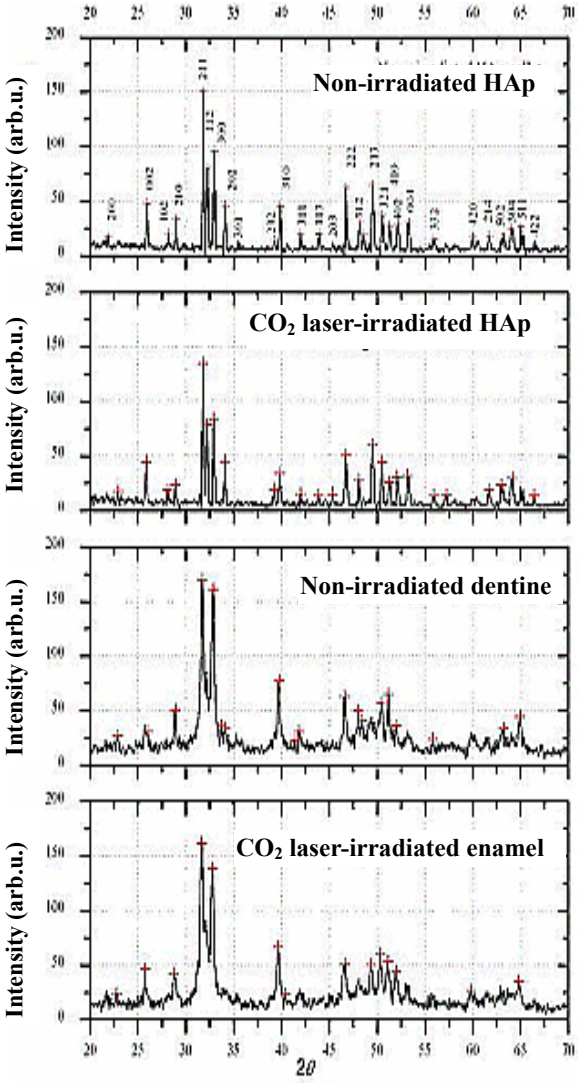

Figure 2: Comparison of CO_2 laser irradiation on artificial HAp and dentine sample

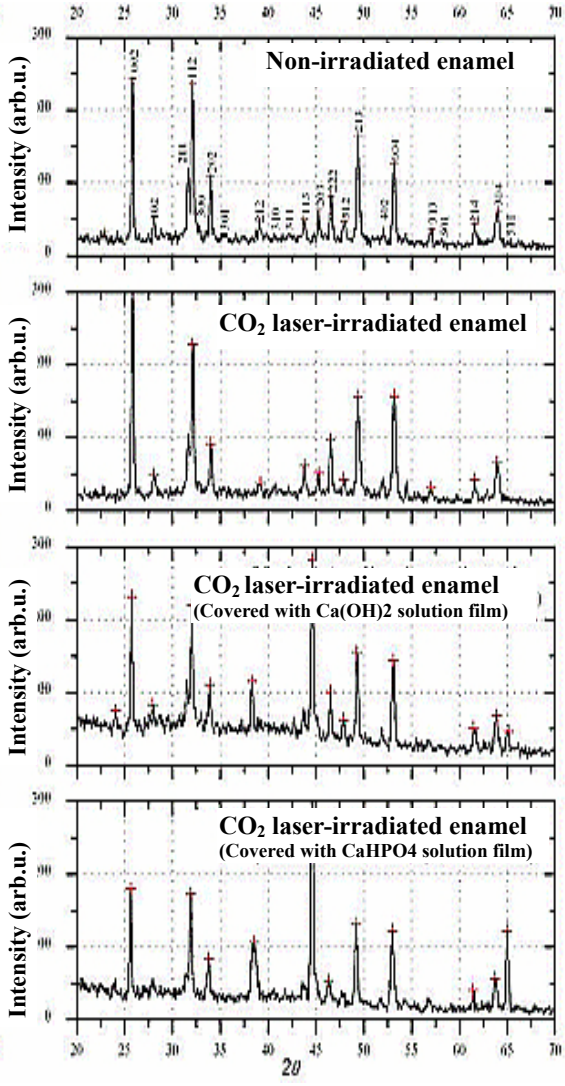

Figure 3: Comparison of CO_2 laser irradiation on enamel sample, with and without chemical solution

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 and dentine. It was considered relating to the thermal effect during high-energy irradiation.

The intense band in the spectrum around 2θ=45° (fig.3) is not a HAp band, but a strong metal reflection most possibly caused by aluminum. In the some observation, this band has been erroneously assigned as a HAp band in the XRD spectra of phosphates. In the spectrum of irradiated samples, the crystal phase show very broad peaks and high background. This may indicate the presence of very small crystallites, which will result in broad peaks.

The broadening of spectrum was assumed to be caused mainly by crystallite (domain) and lattice strain (within the domain). At the same time, we can see the new peaks, which indicate HAp did not dissociate, but is transformed to a new ablated form about 1000 degree. Phase transition in $Ca_3(PO_4)_2$ from a tricalcium phosphate type to a HAp type structure, which also occurs at the similar conditions, did not induce the dissociation of HAp. However, we were failed to assign the new peaks to these structures. Alternatively, the diffraction peaks of a new HAp polymorph can be indexed by an orthorhombic cell with lattice parameter a=b=9.43nm, c=0.688nm.

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