Sains Indonesia Vol. 8, No.1 (2003) 9-12

Crystallite Size and Micro Strain Studies of Tooth Enamel by XRD

Muhammad Hikam and Rosalina Tjandrawinata
Department of Physics, Faculty of Mathematics and Sciences, University of Indonesia
Depok 16424 Indonesia

Abstract

The purpose of this experiment is to study the influence of 10% carbamide peroxyde and 0.4% stannous fluoride application on the crystallite of hydroxyapatite in tooth enamel, by using x-ray diffraction method. Hydrogen peroxide solution and distilled water are used as control. The materials are applied for 8 hours in an incubator with 37°C and 100% humidity, for total 192 hours. The crystallite size and the lattice parameters are calculated from x-ray diffraction pattern, and the structure was then refined by Rietveld analysis. It can be concluded that carbamide peroxyde and stannous fluoride do not influence neither the crystallite size of tooth enamel nor the lattice parameters, but they influence the micro strain in crystal. The x-ray diffraction on the facial surface of enamel shows preferred orientation pattern at [002].

Keywords: tooth enamel, crystallite size, micro strain, XRD

1. INTRODUCTION

Most commercial dental whiteners contain hydrogen and carbamid peroxydes. One can use carbamid peroxyde at home personally with a periodical control of a dentist. This material is placed on a nightguard or a tray to support and keep in contact with the treated teeth [1].

In whitening dental treatment, side effect could occur in the form of rough sensation and increasing sensitivity to temperature. This effect might not be a direct result of the whiteners but from erosion, attrition or aberration of the teeth. In the usual medical practice, this effect is remedied by fluor. In the dental tissue, flour is confined in form of CaF_2 that prevents dissolution of enamel hydroxy-apatite crystal due to aliments or acids in the mouth [2]. It could also prevent demineralization by forming flouro-apatite:

$$F + Ca_5(PO_4)_3(OH) \rightarrow Ca_5(PO_4)_3F + [OH]^- \quad (1)$$

Tooth enamel has organic matrix of which anorganic compound is less than 90% in the form of calcium hydroxy-apatite $Ca_5(PO_4)_3(OH)$ or $Ca(OH)_2.3Ca_3(PO_4)_2$. It has hexagonal structure [3] with a crystal group of C_6. Meanwhile, Tsuda and Arends [4] using Raman-Micro spectroscopy claimed that the cell unit symmetry was $C^6_6(P6_3)$.

One can use x-ray diffraction method or TEM (Transmision Electron Microscope) to measure the size of crystallite or the grain of calsium hydroxy-apatite. Jensen dan Möller in 1948 had tried to calculate this quantity by x-ray method [5].

In this research we calculated crystallite size and micro strain of several human tooth enamels as the function of utilization of carbamide peroxyde and stannous flouride. Knowing the changes of these quantities as a result of employing these whitener's materials, we could anticipate the mechanical properties that cause the degradation of dental material and we would get the understanding on how to reduce the side effect of these whiteners.

2. CRYSTALLITE SIZE AND MICRO STRAIN CALCULATION

The crystallite size of a material can be calculated basically by using peak widening at a certain diffraction point. Scherrer [6] and Wijaya et al. [7] had shown that the relationship between curve widening (β) and crystal grain dimension (D) at the angle θ and x-ray wavelength λ is:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

where K is a constant, its value (normally from 0.70 until 1.70) depends on crystal form and Miller indices *hkl* [8].

In equation (2), Scherrer had assumed the non existence of micro strain and defect material, therefore the peak widening is only due the size of crystallite [9]. Apart from the crystallite size, instrumental curve widening always exists on account of finite slits, sample size, sample transperancy and unfocused ray. Further widening could be the result of at K_α doublet. This instrumental curve widening can be estimated by using

a powder specimen standard that has large particle size to eliminate crystallite widening [9]. Warren proposed the following relation:

$$B^2 = \beta^2 + b^2 \qquad (3)$$

where β is curve widening due to grain size, B is curve widening after K_α doublet correction and b is instrumental curve widening.

In general, peak widening consists of widening due crystallite size (β_c) and micro strain (β_s):

$$\beta = \beta_c + \beta_s \qquad (4)$$

Crystallite size peak widening can be written (2):

$$\beta_c = \frac{K\lambda}{D\cos\theta}.$$

While micro strain peak widening is

$$\beta_s = \eta \tan\theta. \qquad (5)$$

Hence, the total peak widening can be written as summing of these termes:

$$\beta\cos\theta = \frac{\lambda}{D} + \eta\sin\theta \qquad (6)$$

by taking $K = 1$ [9, 13].

3. EXPERIMENT

We have used the following apparatus to examine tooth enamel specimen properties:

- Philips Analytical Diffractometer PW3710.
- SEM (Scanning Electron Microscope)
- Dental preparation apparatus: micromotor, straight handpiece, air jet handpiece, diamond bur.
- Freezer
- Incubator 37°C.
- Square glass 20 x 20 cm.

The materials and chemicals used in the experiment are the following:

- Dental materials. These specimens were cleaned to remove the blood stained and were kept in distilled water at temperature of 4° C.
- Stannous fluoride Gel (SnF_2) 0.4 %, from Stan-Gard of Pascal
- Carbamid peroxyde Gel ($CH_4N_2OH_2O_2$) 10 %, from Opalescence of Ultradent.
- Hydrogen peroxyde solvent (H_2O_2) 10 %
- Distilled water
- Alcohol (70%) for fat cleansing
- Quartz powder as standard specimen.

We began the experiment by scanning quartz specimen to standardize the apparatus and to obtain the instrumental factor of peak widening. The diffractometer was set:

- source : CoKα
- voltage : 35 kV
- current : 20 mA
- scan speed : 1.5 °/minute
- 2θ range : 20° - 80°

Our specimens were then scanned on the similar condition. After taking x-ray data for untreated samples, we classify and process the samples into 5 categories:

A. Specimen was immersed in SnF_2 0.4% for 8 hours duration. It was then cleaned by distilled water. The specimen was immersed again in SnF_2 0.4% for 8 hours, cleaned again until the total time was 48 hours.

B. Specimen was immersed in carbamide peroxyde 10% for 16 hours and the solvent was renewed after the first 8 hours. The specimen was then cleaned and immersed in distilled water. The process was repeated until the total immersion time in carbamide peroxyde 10% for was 96 hours and in distilled water was 48 hours.

C. Specimen was immersed first in gel carbamide Peroxyde 10% for 16 hours followed by distilled water in 8 hours and SnF_2 0.4% in 8 hours. Fresh distilled water was used for 8 hours. The process was repeated until we obtained the immersion time in carbamide Peroxyde was 96 hours and in SnF_2 0.4% was 48 hours.

D. Specimen was immersed in hydrogen peroxyde 10% for 16 hours and the solvent was renewed every 8 hours. After cleaning with distilled water, the specimen was kept in the water for 8 hours. The process was repeated until the total immersion time in hydrogen peroxyde 10% was 96 hours and in distilled water was 48 hours.

E. Specimen was immersed only in distilled water for 8 hours. The solvent was changed and the specimen was immersed again until total time of 96 hours.

All the A, B, C, D, and E steps were done in an incubator 37°C. After these ABCDE steps we took x-ray data for each of them. Then the ABCDE steps were repeated again for the respective speciments and the final results were also examined by x-ray. On that account we obtained three diffraction data for each specimen.

All the diffraction data were treated individually by fitting to remove the background then the curve widening was corrected by instrumental factor. As mentioned before a quartz crystalline was used to calibrate this factor.

4. RESULTS AND ANALYSIS

Figure 1 shows the x-ray diffraction pattern of the specimen 14EMB (category B). Beside ABCDE classification, we differentiate also the specimen examined in the dentine area direction and in the facial direction. We found that the tooth enamel in labial section has curve widening smaller than the one in dentinoenamel junction.

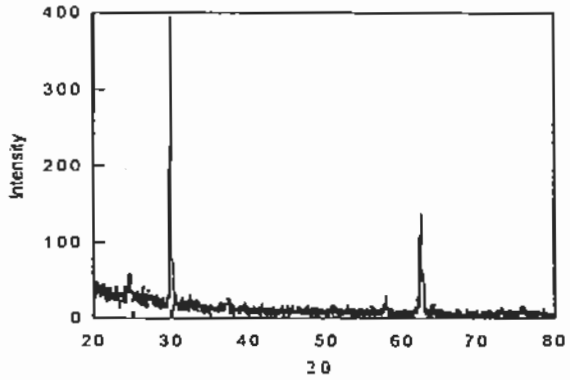

Fig. 1. X-ray diffraction pattern of tooth enamel (Em14B)

We have employed the APD (*Automatic Powder Diffraction*) program to calculate d-spacing and the curve widening. By using the usual relation of d-spacing and tetragonal lattice constants [11]:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}, \quad (7)$$

We obtain the following lattice parameters of hydroxy-apatite crystal for the outer tooth enamel: $a = (9.456 \pm 0{,}043)$ Å and $c = (6.888 \pm 0.006)$ Å, and for inner tooth enamel: $a = (9.434 \pm 0{,}035)$ Å and $c = (6.890 \pm 0{,}004)$ Å. The differences are not significant.

A Rietveld program written by Li [12] was then used to refine the data. The lattice parameters do not vary greatly, while the preferred orientation depends on the sample. For the facial direction the hydroxy-apatite crystal has the tendency to the 002 direction while in the dentino junction there is no special preferred orientation. Although the 112 direction was suggested by the program for the later case but we think that there is no ground for that direction.

Close discussion for the ABCDE categories are the following:

In the group A in which the specimen immersed in SnF_2 0.4%, the diffraction pattern does not change. This result is similar to those of Wei's research [2] where he treated an original tooth enamel (not in powder form) using NaF or flouride acid solvent. Meanwhile in the second group (B) where the specimen immersed in gel carbamide peroxyde, the angle of diffraction does not change, however the peak intensity at $2\theta = 30°$ (002 plane) decreases on the treatment, the same thing happen at $2\theta = 62°$ (421 plane). In the group C where the specimen immersed alternatingly in carbamide peroxyde and stannous fluoride solvents, we observe no significance change. Speciment in the category D was immersed in hydrogen peroxyde solvent. The 002 peak decreases on treatement. In the last group (E) the speciment was immersed in distilled water and the two side of the sample was examined. We found that the peak diffraction on the facial enamel was highest at the direction of the preferred orientation 002, but that was not the case in the dentino enamel junction.

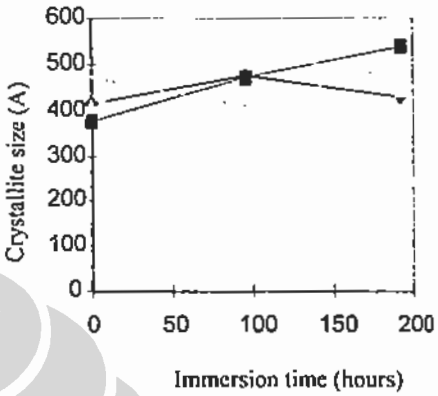

Fig. 2. Change of crystallite size on immersion in carbamide peroxyde

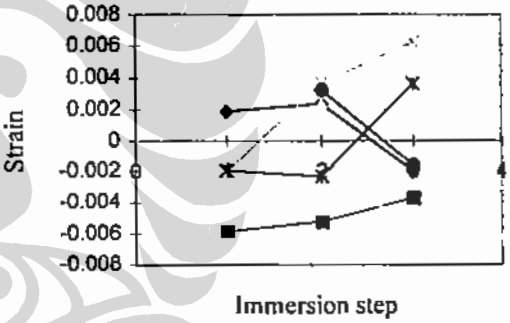

Fig. 3. Strain change due to immersion in carbamide peroxyde, measured at 421 plane.

When we calculated the crystallite size, we obtained that this quantity is not uniform. In the direction of preferred orientation (002) for labial section the value is 421 ± 61 Å while for dentino enamel junction the crystallite size is 438 ± 92Å.

There are no significance variation of crystallite size after immersion process in whitener materials. Figure 2 shows these changes. On the contrary, we found that the micro strain varies in very significance matter when the materials were treated by the whiteners. Figure 3 shows the process.

The SEM [*Scanning Electron Microscope*] results show that the facial tooth enamel is coarser and more porous as the effect whitener materials both carbamide peroxyde and hydrogene peroxyde. This porous effect could be lessen by using stannous flouride, nevertheles the original form could not be recovery.

5. CONCLUSION

We can conclude that the use of two whiteners, carbamide peroxyde plus hydrogen peroxyde and stannous flouride do not have any influence on the structural crystallographic system and crystallite size of hydroxy-apatite. They have certain influence on the micro strain of the crystal.

The x-ray diffraction results show that all the hydroxy-apatite crystals from the tooth enamel are hexagonal, similar to the one obtained in nature. The lattice contants do not vary eminently (± 0,04 Å). The preferred orientation is in the 002 plane.

Taking a close look at the diffraction pattern, we found that the diffraction peaks of the specimen examined in the dentine area direction were wider but smaller compared with the data taken in the facial direction. This result shows us that the degree of crystalinity of hydroxy-apatite in the facial direction is higher than the one in dentine area.

REFERENCES

[1] Newman, S.M., Bottone, P.W. 1995. Tray Forming Technique for Dentist-supervised Home Bleaching. *Quintessence Int.* 26. 447 - 453.

[2] Wei, S.H.Y., Forbes, W.C. 1968. X-Ray Diffraction Analyses of the Reactions Between Intact and Powdered Enamel and Several Fluoride Solutions. *J Dent Res.* 47 (3). 471 – 477.

[3] Ten Cate, A.R.1985. *Oral Histology : Development, Structure and Function.* The C.V. Mosby Company. St. Louis. 2nd ed. 183 – 216.

[4] Tsuda, H., Arends, J. 1994. Orientational Micro-Raman Spectroscopy on Hydroxyapatite Single Crystals and Human Enamel Crystallites. *J Dent Res.* 73 (11). 1703 – 1710.

[5] Kerebel.B., Daculsi, G., Kerebel, L.M. 1979. Ultrastructural Studies of Enamel Crystallites. *J Dent Res.* 58 (B). 844 - 850.

[6] Klug, H.P., Alexander, L.E. 1974. *X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials.* John Wiley & Sons, Inc. 2nd ed. 635 – 657.

[7] Wijaya, S.K., Tjandrawinata, R., Parangtopo. 1996. Penggunaan XRD untuk Penghitungan Ukuran Kristalit, Studi Kasus pada SiC. *Prosiding Pertemuan Ilmiah Sains Materi BATAN.* 372 - 378.

[8] Bartram, S.F. 1967. Crystallite Size Determination from Line Broadening and Spotty Patterns in *Handbook of X-Ray* (ed. by E.F. Kaelble). Mc. Graw Hill. New York.

[9] Warren, B.E. 1990. *X-Ray Diffraction.* Dover Publication Inc. New York. 1st ed. 251 – 312.

[10] Tamura, K., Mori, M., Kawakatsu, K. 1971. A Comparative Study of X-ray Diffraction and Infrared Absorption Properties and Amino-acid Analysis of B ovine Enamel. *Arch Oral Biol.* 16. 801 - 811.

[11] Cullity, B.D. 1978. *Elements of X-ray Diffraction.* Addison-Wesley Publishing Company Inc. Massachusets. 2nd ed. 502, 517

[12] Li D.Y., Li J.Y. and O'Connor B.H., 1991. *Program PCRTVW-A PC Version Of Rietveld Program LHPM10 and Associated Program Weight For Phase Analysis,* Seventh State Conference AXAA, 21-22 September