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Effect of Sodium Fluoride-Hydrofluoric Acid Systems on Dentin of Human Molars

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ABSTRACT

Fluoride is known to react with dental dentin to produce calcium fluoride or fluorapatite to close dentin tubules to treat hypersensitivity. However, the formation of calcium fluoride or apatite is common in the recurrent disease, with rapid disappearance by mechanical or acidic stimuli. We have focused our attention on the fact that the newly developed NaF-HF gel has high chemical reactivity and a rapid rate of calcium fluoride formation in response to dental inorganic substrates and have chosen the research project to investigate the effect of this fluoride on human dental dentin. The main reaction product on fluoride-applied human molar dentin surfaces is fluoride apatite, whose production is enhanced by the number of fluoride applications and gelatinization is higher than that of the solution. When fluoride is applied and acid and mechanical stimulation is applied 28 days after immersion in artificial saliva, the acid stimulation has a greater effect on human molar dentin tubule closure than mechanical stimulation.

Keywords: Hypersensitivity, Naf-HF Solution Or Gel, Dentin, Molar, Fluorapatite, Calcium Fiuoride.

Article Information

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INTRODUCTION

The causes of dentin hypersensitivity include the abrasion of the dental cervical region by applicationing teeth, the abrasion of the masticatory surface by mastication, erosion, dental cutting for restoration, and the dental root exposure by periodontal disease, and periodontal treatment and tooth bleaching including scaling, dental root surface lubrication, etc.[1, 2, 3]. It has also been reported that taking the acidic foods or beverages leads to a progressive increase in sensitivity, exposing dentin tubules [4]. Histologically, hypersensitive dentin has a greater opening of dentinal tubules compared to non-hypersensitive dentin, suggesting that tissue fluid can move freely between the pulp and oral sides of dentinal tubules. Hypersensitivity has been reported to be closely related to tubule openness [5]. Scanning electron microscopic examination

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of hypersensitive spot or hypersensitive zone of teeth with dentinal hypersensitivity has shown that the dentin tubules in this area are enlarged or tubular (6).

Hypersensitivity occurs only partially in the region with open tubules on the dentinal surface, where tubules have a wider entrance and a greater number of open tubules than in the non-hypersensitive region [7]. Some researchers have reported that mechanical closure of the open tubules reduces dentinal permeability and hypersensitivity, and hypersensitivity continues unless tubular is close [8]. Treatments for dentinal hypersensitivity are based on the reduction of the dentinal permeability of external stimuli and maintenance of the occlusion effect when dentin is worn by acid induction and toothapplicationing [9].

Sodium fluoride has been widely used as a anti-hypersensitive drug since 1943[10,11]. Although sodium fluoride reduces dentinal permeability in a short period[12], some studies have shown that the mode of action of fluoride is to precipitate the calcium fluoride crystals and close the tubules, which may be removedby saliva and toothapplicationing [14]. Fluoride as an anti-dentinal hypersensitivity agent reacts with dentin in teeth to form the insoluble calcium fluoride and fluoroapatite[15], which closes dentinal tubules. Fluoride is mainly used as the forms of sodium fluoride paste, fluoride varnish, fluorine paste, and sodium fluoride solution [16]. A researcher examined the effect of the combined application of mono sodium fluophosphate and APF on the dentinal corrosion. The results of the experiments showed that the combined application of mono sodium fluophosphate and APF was most effective in preventing nitric acid-induced dentinal corrosion [17]. However, the effectiveness of sodium fluoride was not high and to overcome this, the use of aminohexafluorosilicon(SiF) has been investigated. When the dentin was treated with SiF, the dentinal tubules were closed completeiy, the dentin didn't dissolve even when treated with 50% citric acid, and the dentinal permeability reduced to 90%[18]. It has reported that fluoride application can react with dental dentin to form water-insoluble calcium fluoride and fluorapatite to close dentinal tubules, but the recurrence rate is high because theses insoluble crystals are easily broken by mouthwash, toothapplicationing, and mastication[19].

However, silver diamine fluoride solution developed as a caries vaccine was used for the treatment of hypersensitivity, since unlike the reports, the therapeutic effect of fluoride application was not so high [20]. Silver diamine fluoride has little effect on pulp, and reacts with dentin to form insoluble silver phosphate and calcium fluoride to close dentin tubules, with a therapeutic effect of 41%, a drug effect of 32%, and an ineffectiveness of 27%[16]. It has reported that Silver diamine fluoride is effective to the treatment of the caries of adult people, especially the treatment of periodontal caries and hypersensitivity. Silver diamine fluoride has a high reduction effect on temperature-induced pain because it results in closure of dentinal tubules, but it has the disadvantages that it discolorates the teeth or stimulates and erodes gingival tissue [21,22,23]. Recently, we have developed a new fluoride, NaF-HF gel. This fluoride has a higher chemical reactivity with hydroxyapatite compared to other fluorides, resulting in a faster rate of calcium fluoride formation. Therefore, it has reported that it has also a high caries prevention effect[24,25]. However, the effect of this fluoride on dentinal hypersensitivity has not been elucidated. Our objective was to examine the reaction products on fluoride-applied human molar dentin surfaces and to determine the changes of the reaction products in human molar dentin pieces after acid and mechanical stimulation.

MATERIALS AND INSTRUMENTS

1. Teeth

The human mandibular third molar drawn in due to periodontal disease was cleaned and stored in 0.5% thymol solution at 4 °C until use. A diamond disk was used to cut vertically to the longitudinal axis of the tooth from the cement-enamel interface. The coronal enamel was then ground to expose the dentin. The top surface of the piece is enamel-side and the bottom surface is a disk oriented toward the pulp chamber.

2. Chemical agents

① 6% Citric acid solution(analytical grade, pH 1.82)
② Sodium chloride(analytical grade)
③ Potassium chloride(analytical grade)
④ Calcium chloride(analytical grade)
⑤ Magnesium chloride(analytical grade)
⑥ Sodium hydrogen phosphate(analytical grade)
⑦ Potassium hydrogen phosphate(analytical grade)
⑧ Sodium bicarbonate(analytical grade)
⑨ Glucose(purified product).

Table1.The composition of artificial saliva(Gey's solution)[①②17]

Sodium chloride(NaCl)	g	8.00
Potassium chloride(KaCl)	g	0.38
Calcium chloride($CaCl_2$)	g	0.13
Magnesium chloride($MaCl\cdot6H_2O$)	g	0.21
Sodium hydrogen phosphate($NaHPO_4\cdot12H_2O$)	g	0.30
Potassium hydrogen phosphate(KH_2PO_4)	g	0.025
Sodium bicarbonate($NaHCO_3$)	g	1.0
Glucose	g	0.25
Water	L	rest
Total	L	1

3. Fluorides

① Sodium fluoride-hydrofluoric acid solution with 1.23% F^-(1.23% NaF-HF solution)

NaF-HF solution with 1.23% F^- was prepared by dissolving 1.5g of NaF and 1.60mL of 40% HF with 0.608g of F^- into distilled water and adjusting total volumn to 100mL.(pH 3.72)

② APF solution with 1.23% F^-(1.23% APF solution)

APF solution was prepared according to the following procedure as described in the literature. 2g of sodium fluoride were dissolved in 99.175 mL of 0.1M orthophosphoric acid in a polyethylene plastic container and then, 0.825mL of 40% hydrofluoric acid(0.33g F^-) was added. pH of APF solution was 3.0.

③ Sodium fluoride-hydrofluoric acid gel with 1.23% F^-(1.23% NaF-HF gel)

NaF-HF gel with 1.23% F^- was prepared by dissolving 1.5g of of sodium fluoride, 1.60mL of 40% hydrofluoric acid (0.608g F^-), and 3.0g of CMC in the distilled water and adjusting total volumn to 100 mL. pH of APF gel was 5.67.

④ distilled water

4. INSTRUMENTS

① Dental application("PaeHak" brand application with the bristle yarn of 0.17mm)
② X-ray diffraction apparatus(XRD, D8 ADVANCE, Nederland)

③ Scanning electron microscope(SEM, Quanta 200)

METHOD

1. Products of reaction on dentinal surface of human molar

The dentinal surfaces of all pieces were treated with 6% citric acid for 30s to remove the contamination layer, each fluorides and distilled water were applied on the pieces for 4 min, and then they were washed and dried with deionized water and ultrasound. After the application of fluorides, X-ray diffraction(XRD) analysis on the dentin pieces was performed to identify the reaction products and then Rietveld analysis was performed. Also, Scanning electron microscope (SEM) analysis was performed.

2. The change of reaction products in dentin pieces of human molar after the pieces were exposed to fluorides, put under artificial saliva, and received acidic and mechanical stimulation

All pieces were exposed to fluorides for 4 min and immersed in artificial saliva for 28 days at 37 °C without washing. The artificial saliva was replaced daily. All pieces were taken in duplicate, one piece was treated with 6% citric acid solution for 1 min, and the other piece was subjected to acid stimulation by applicationing. The mechanical stimulation was given by making the bristle of the "Paekhak" toothapplication with 0.17 mm bristle touch the surface of piece vertically and applicationing at 300 rpm for 2 min by a trained examiner [27]. XRD and SEM analysis were performed after acidic and mechanical stimulation.

XRD and SEM analysis

① XRD analysis of dentinal surface of fluoride-applied human molar.

The pieces were measured by X-ray diffraction(XRD) apparatus(D8 ADVANCE, Nederland), a Bruker AXS D8 ADVANCE powder diffractometer with a CuKa1 characteristic line(λ=1.540 6Å) controlled at 45kV and 40mA in the scanning range of 20° to 80° with a step interval of 0.02°/0.5. The qualitative analysis of the X-ray measurement data was carried out with the EVA program and Rietveld refinements of crystal structures were performed by TOPAS 3.0 programme using the database of ICSD(Inorganic Crystal Structure Database).

② Scanning electron microscopy (SEM) analysis of dentinal surface of fluoride-applied human molar

All the pieces examined above were observed by using SEM. A high-purity carbon material-based conductive strip with adherence on double sides was attached on a aluminum stud with 7 mm diameter to set pieces, and the molar dentin pieces were fixed on the conductive strip and then sputtered. The sputtering voltage was 46mV, the distance from the piece to the anti-cathode was 60 mm, the sputtering time was 2 min, the vacuum degree was 0.1Pa, and platinum was used as the anti-cathode. The sputtered piece was analysed by using SEM at 20kV.

RESULTS

1. Reaction products on dentin surfaces of NaF-HF-applied human molar

1) Reaction products on dentin surfaces of human molar immediately after application of different fluorides

CaF_2, FA and HA diffraction lines were observed in all fluoride-applied pieces. In addition, they were observed in the distilled water-applied piece.

Figure 1 shows Rietveld analysis of fluoride-applied dentin surface.

Table 2 shows the CaF_2, FA and HA contents of different fluorides-applied dentin pieces.

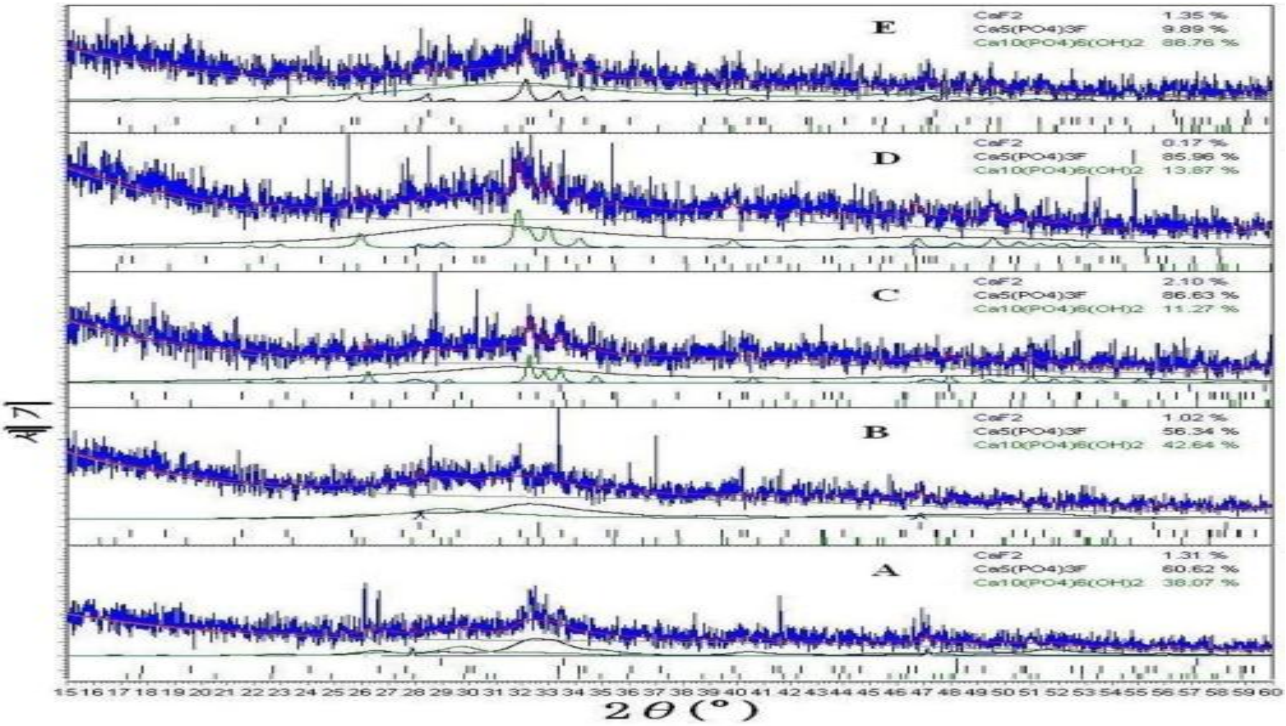

Figure1. Rietveld analysis of different fluorides-applied dentin pieces.

A: one application of 1.23% NaF-HF gel B: one application of 1.23% NaF-HF solution C: two application of 1.23% NaF-HF solution- D: Three application of 1.23% NaF-HF solution E: one application of 1.23% APF solution.

Table 2 shows the CaF_2, FA and HA contents of different fluorides-applied dentin pieces. the content of fluoroapatite formed on the dentin surface was 60.62% in the piece with one application of the 1.23% NaF-HF gel, 56.34% in the piece with one application of the 1.23% NaF-HF solution, 76.63% in the piece with two applications of the 1.23% NaF-HF solution, 85.96% in the piece with three applications of the 1.23% NaF-HF solution, 9.89% in the piece with one application of APF solution and 29.93% in the piece with one application of the distilled water.

HA content was 38.07% in the piece with one application of the 1.23% NaF-HF gel, 42.64% in the piece with one application of the 1.23% NaF-HF solution, 21.27% in the piece with two applications of the 1.23% NaF-HF solution, 13.87% in the piece with three applications of the 1.23% NaF-HF solution, 88.76% in the piece with one application of APF solution and 69.99% in the piece with one application of the distilled water. Meanwhile, CaF_2 content was 1.31% in the piece with one application of the 1.23% NaF-HF gel, 1.02% in the piece with one application of the 1.23% NaF-HF solution, 2.10% in the piece with two applications of the 1.23% NaF-HF solution, 0.17% in the piece with three applications of the 1.23% NaF-HF solution, 1.35% in the piece with one application of APF solution and 0.08% in the piece with one application of the distilled water.

In the control piece, the major inorganic substance was HA, which accounted for most, 69.99% of the surface of human molar dentin, whereas after the application of fluorides, the major component of the reaction products on the surface of human molar dentin was FA and HA most, and the HA content was varied with the change of FA content. That is, the reaction product was found to be FA. FA content was highest in the pieces with 2 and 3 applications of 1.23% NaF-HF solution. FA content in the single-application pieces decreased in order the piece with one application of 1.23% NaF-HF gel, the piece with one application of 1.23% NaF-HF solution, and the piece with one application of 1.23% APF. This indicates that the number of fluoride application affects the FA content of dentin pieces. On the other hand, the FA content in the single-application pieces was less in the NaF-HF solution than that of NaF-HF gel. This means that the fluoride gel formulation is more effective than the solution formulation.

Table 2. The CaF_2, FA and HA contents of dentin pieces immediately afterappling different fluorides(wt%).

Fluorides	One application of 1.23% NaF-HF gel	One application of 1.23% NaF-HF solution	Two applications of 1.23% NaF-HF solution	Three applications of 1.23% NaF-HF solution	One application of 1.23% APF solution	One application of distilled water
CaF_2	1.31	1.02	2.10	0.17	1.35	0.08
FA	60.62	56.34	76.63	85.96	9.89	29.93
HA	38.07	42.64	21.27	13.87	88.76	69.99

2) SEM images immediately after fluoride application

As you can see in SEM images of the dentin pieces of the human molar treated with distilled water in **photo 1**, all tubules were completely open and no phase with closed entrance of the tubule was found. As shown in **Fig. 1**, in all fluoride-applied pieces, dentin tubules were not visible and a blocked phase by the reaction products with fluoride was observed. In the APF-applied piece, dentinal tubules were not completely closed and the tubule entrance was visible, showing relatively incomplete closure compared to other pieces. The dentinal tubules of the control group were completely open.

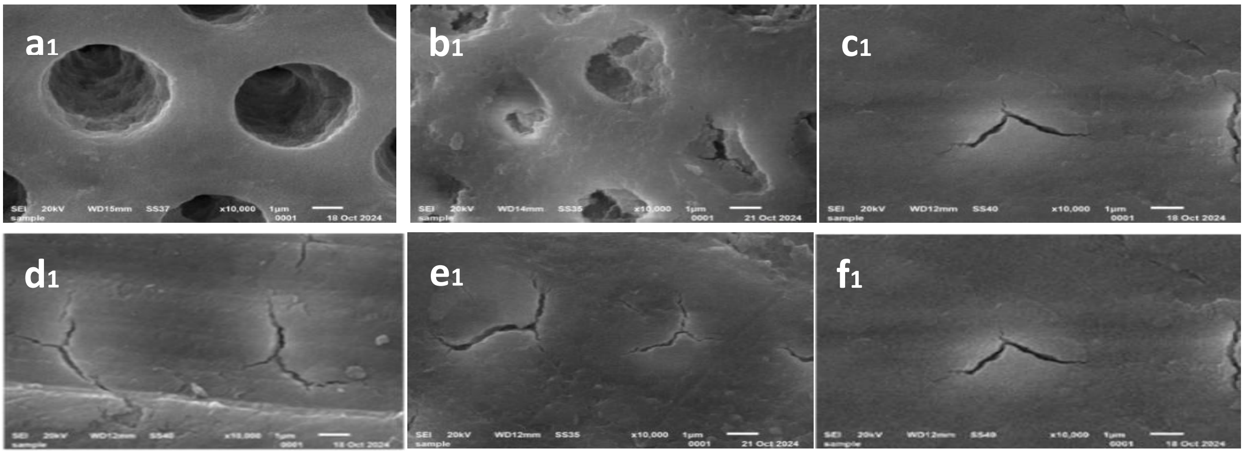

Photo 1. SEM images immediately after applications of different fluorides.

a_1: control group b_1: SEM image of the dentin piece of human molar with one application of 1.23% APF solution c_1: SEM image of the dentin piece of human molar with one application of 1.23% NaF-HF gel d_1: SEM image of the dentin piece of human molar with one application of 1.23% NaF-HF solution e_1: SEM image of the dentin piece of human molar with two applications of 1.23% NaF-HF solution f_1: SEM image of the dentin piece of human molar with three applications of 1.23% NaF-HF solution.

2. Changes of reaction products in acidic and mechanical stimulation-received human molar dentin pieces after fluoride applications and immersion in artificial saliva for 28 days

(1) Reaction products of human molar dentin pieces after fluoride applications and immersion in artificial saliva for 28 days. **Fig. 2** shows Rietveld analysis results in fluoride-applied dentin surface.

Table 3 shows the contents of CaF_2, FA and HA in fluoride-applied dentin pieces

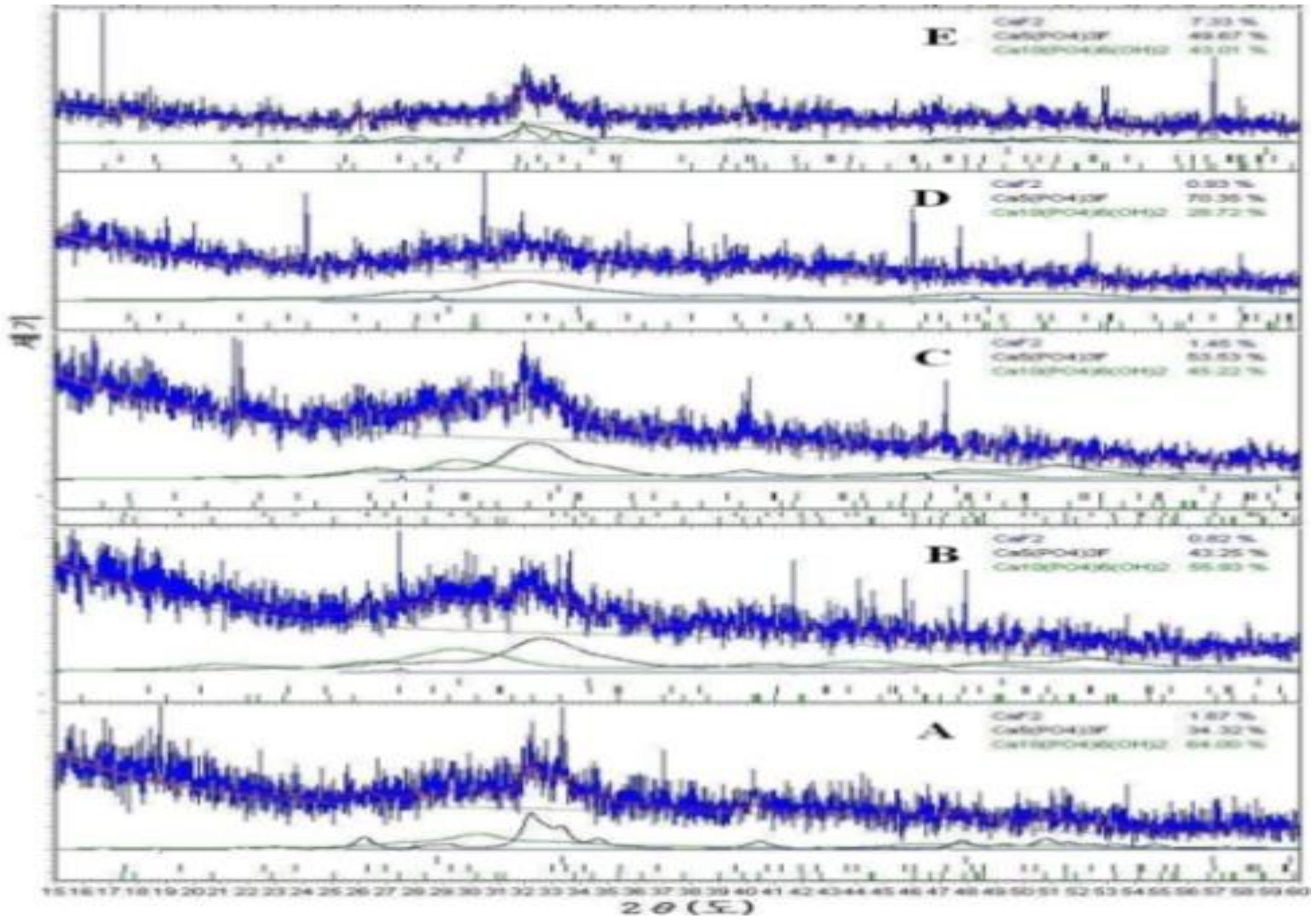

Figure2. Rietveld analysis in fluoride-applied dentin surface

A: one application of 1.23% APF solution B: one application of 1.23% NaF-HF solution C: two applications of 1.23% NaF-HF solution D: three applications of 1.23% NaF-HF solution E: one application of 1.23% NaF-HF gel.

Table 3 shows the contents of CaF_2, FA and HA in fluoride-applied dentin pieces, the content of FA formed on the dentin surface was 60.25% in the piece with one application of the 1.23% NaF-HF gel, 43.25% in the piece with one application of the 1.23% NaF-HF solution, 53.53% in the piece with two applications of the 1.23% NaF-HF solution, 70.35% in the piece with three applications of the 1.23% NaF-HF solution, and 34.32% in the piece with one application of APF solution. The content of HA was 39.70% in the piece with one application of the 1.23% NaF-HF gel, 45.22% in the piece with one application of the 1.23% NaF-HF solution, 55.93% in the piece with two applications of the 1.23% NaF-HF solution, 28.72% in the piece with three applications of the 1.23% NaF-HF solution, and 64.00% in the piece with one application of APF solution.

Meanwhile, the content of CaF_2 was 0.05% in the piece with one application of the

1.23% NaF-HF gel, 0.82% in the piece with one application of the 1.23% NaF-HF solution, 1.45% in the piece with two applications of the 1.23% NaF-HF solution, 0.93% in the piece with three applications of the 1.23% NaF-HF solution, and 1.67% in the piece with one application of APF solution.

Table 3. The contents of CaF_2, FA and HA in fluoride-applied dentin pieces(wt%).

Contents	one application of 1.23% NaF-HF gel	one application of 1.23% NaF-HF solution	two applications of 1.23% NaF-HF solution	three applications of 1.23% NaF-HF solution	one application of 1.23% APF solution
CaF_2	0.05	0.82	1.45	0.93	1.67
FA	60.25	43.25	53.53	70.35	34.32
HA	39.70	45.22	55.93	28.72	64.00

(2) Changes of reaction products after acidic stimulation

① Rietveld analysis after acid stimulation on fluoride-applied dentin surface. Fig. 3 shows Rietveld analysis results after acid stimulation on fluoride-applied dentin surface. **Table 4** shows the contents of CaF_2, FA and HA after acidic stimulation in fluoride-applied dentin pieces.

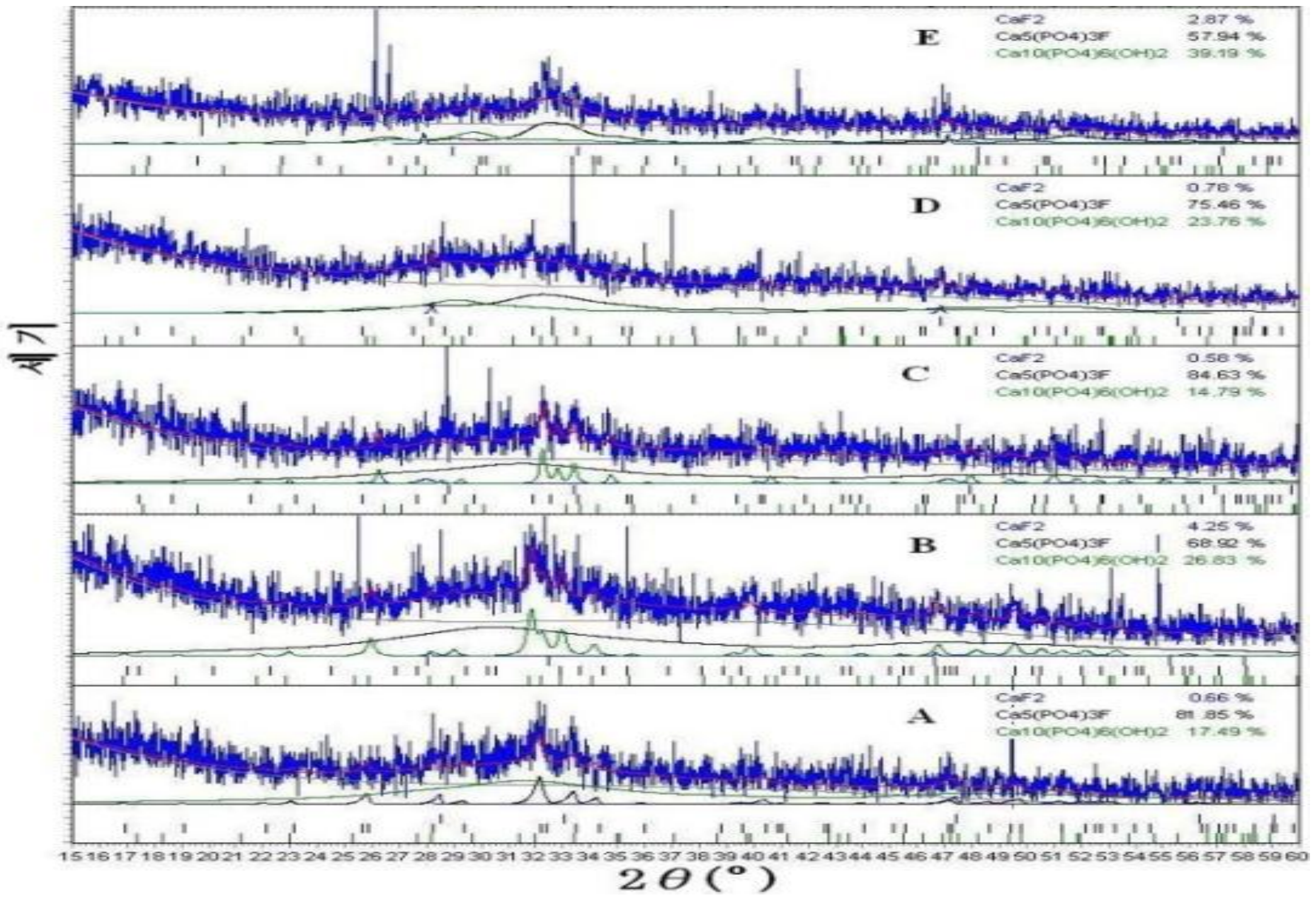

Figure3. Rietveld analysis after acidic stimulation on fluoride-applied dentin surface.

A: one application of 1.23% NaF-HF gel B: three applications of 1.23% NaF-HF solution C: two applications of 1.23% NaF-HF solution D: one application of 1.23% NaF-HF solution E: one application of 1.23% APF solution.

Table 4 shows the contents of CaF_2, FA and HA after acidic stimulation in fluoride-applied dentin pieces, the content of FA formed on the dentin surface after acidic stimulation was 81.85% in the piece with one application of the 1.23% NaF-HF gel, 68.92% in the piece with one application of the 1.23% NaF-HF solution, 57.94% in the piece with two applications of the 1.23% NaF-HF solution, 75.46% in the piece with three applications of the 1.23% NaF-HF solution, and 84.63% in the piece with one application of APF solution.

Table 4. The contents of CaF_2, FA and HA after acidic stimulation in fluoride-applied dentin pieces(wt%).

Fluorides	one application of 1.23% NaF-HF gel	one application of 1.23% NaF-HF solution	two applications of 1.23% NaF-HF solution	three applications of 1.23% NaF-HF solution	one application of 1.23% APF solution
CaF_2	0.66 (0.05)	4.25 (7.33)	2.87 (0.82)	0.78 (1.45)	0.58 (0.93)
FA	81.85 (60.25)	68.92 (49.67)	57.94 (43.25)	75.46 (53.53)	84.63 (70.35)
HA	17.49 (39.70)	26.83 (43.01)	39.19 (45.22)	23.76 (55.93)	14.79 (28.72)

():contents after immersion in artificial saliva for 28days

② SEM images after acid stimulation

Photo 2. SEM images of dentin pieces after acid stimulation(3000-fold magnification). The dentin tubules with round or oval fine entrances completely exposed on the surface of the dentin in the control group are shown. Dentin surfaces with 3 applications(b) and 2 applications(c) with 1.23% NaF-HF solution were not completely exposed after 6% citric acid treatment, and fine pores were seen, with the pore diameter being significantly smaller than that of the control group. On the surface of dentin with a single application with 1.23% NaF-HF gel, the appearance of exposed dentinal tubule was recognized, but the plate inorganic minerals were present at the entrances of tubules in the inners of most tubules, and the entrances were not completely open, and there were small pores in the centers of some tubules. And on the surface of dentin with a single application with 1.23% NaF-HF solution, the appearance of exposed dentinal tubule was recognized, but the diameters of the pores formed in the shallow layers of tubules were significantly smaller than that of the control group, and some pores with large diameter were also seen. Meanwhile, on the surface of dentin with a single application with 1.23% APF solution, dentinal tubules were completely open and the diameters of pores were almost the same as the control group, but the new layers were formed in deep layers of some tubules and small holes were seen in the centers.

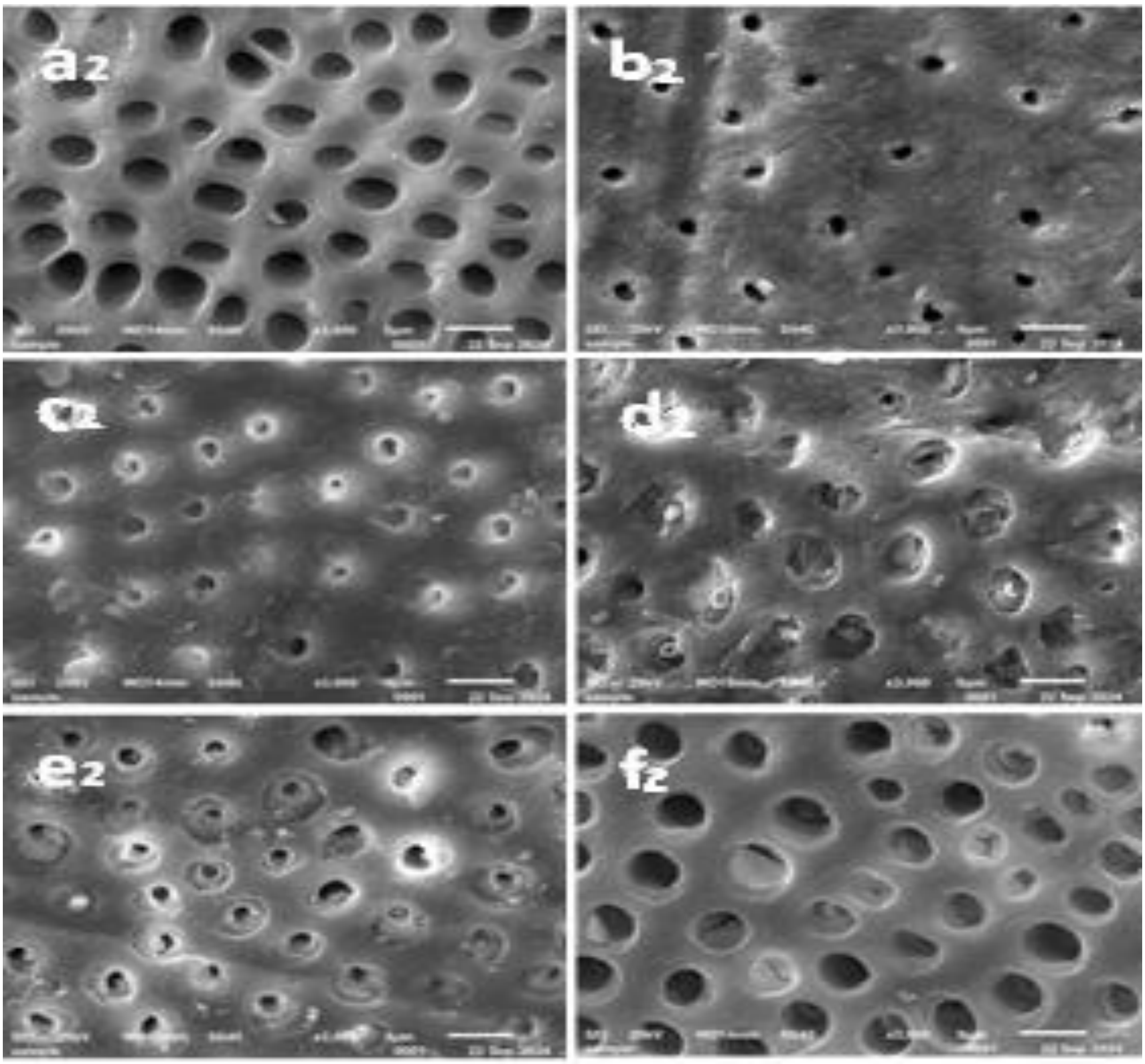

Photo 2. SEM images of dentin pieces after acid stimulation(3000-fold magnification).

a_2: control piece b_2: SEM image of human molar dentin piece with three applications with 1.23% NaF-HF solution c_2: SEM image of human molar dentin piece with two applications with 1.23% NaF-HF solution d_2: SEM image of human molar dentin piece with one application with 1.23% NaF-HF gel e_2: SEM image of human molar dentin piece with one application with 1.23% NaF-HF solution f_2: SEM image of human molar dentin piece with one application with 1.23% APF solution.

2) Changes after mechanical stimulation

① Rietveld analysis of fluoride-applied dentin surfaces after mechanical stimulation

The diffraction lines for CaF_2, FA, and HA were recognized in all fluoride-applied pieces.

Figure 4 shows the Rietveld analysis after mechanical stimulation of the fluoride-applied dentin surface.

Table 5 shows the contents of CaF_2, FA and HA of the dentin pieces treated with fluoride solution after mechanical stimulation.

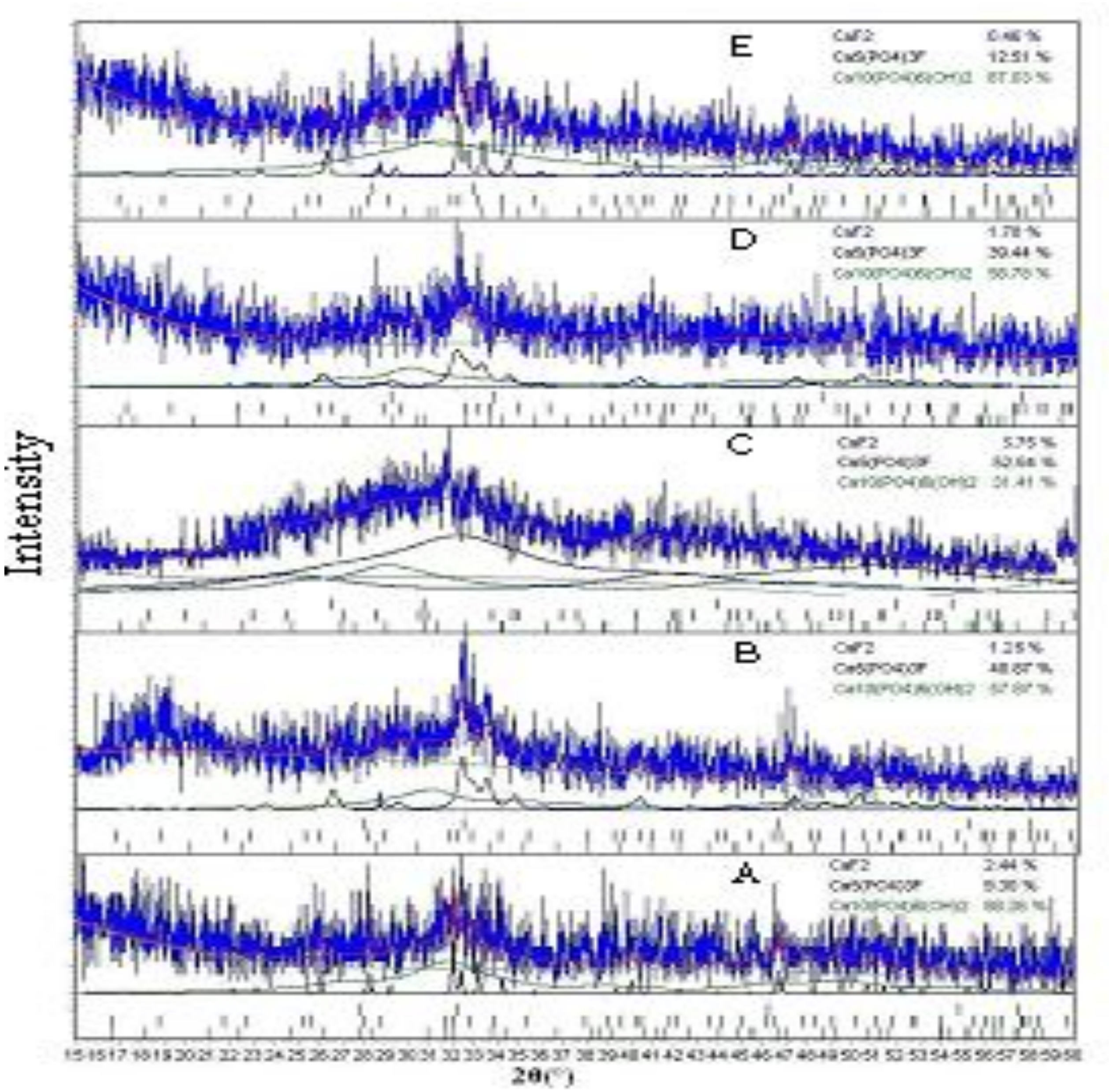

Figure 4. Rietveld analysis of fluoride-applied dentin surface after mechanical stimulation.
A: one application with 1.23% APF solution, B: one applications with 1.23% NaF-HF gel C: three applications with 1.23% NaF-HF solution D: two applications with 1.23% NaF-HF gel E: one application with 1.23% NaF-HF solution.

Table 5 shows the contents of CaF_2, FA and HA of the dentin pieces treated with fluoride solution after mechanical stimulation, the content of FA formed on the dentin surface after mechanical stimulation was 12.51% in the piece with one application with the 1.23% NaF-HF solution, 39.44% in the piece with two applications with the 1.23% NaF-HF solution, 52.84% in the piece with three applications with the 1.23% NaF-HF solution, 40.87% in the piece with one application with the 1.23% NaF-HF gel, 17.13% in the piece with one application with the 0.5% NaF-HF gel, and 9.30% in the piece with one application with 1.23% APF solution.

Table 5. The contents of CaF_2, FA and HA of the dentin pieces treated with fluoride solution after mechanical stimulation(wt%)

Fluorides	one application with 1.23% NaF-HF solution	two applications with 1.23% NaF-HF solution	three applications with 1.23% NaF-HF solution	one application with 1.23% NaF-HF gel	one application with 1.23% APF solution
CaF_2	0.46 (0.82)	1.78 (1.45)	5.75 (0.93)	1.27 (0.05)	2.44 (1.67)
FA	12.51 (43.25)	39.44 (53.53)	52.84 (70.35)	40.87 (60.25)	9.30 (34.32)
HA	87.03 (45.22)	58.78 (55.93)	41.41 (28.72)	57.86 (39.70)	88.26 (64.00)

(): contents after immersion in artificial saliva for 28 days.

As in **photo 3,** the hollow patterns were recognized in the fluoride-applied pieces due to mechanical force of the bristle of the toothapplication, and the hollow striae were parallel to each other. No exposed tubules were seen. The 5000-fold magnification images also showed that the hollow striae were parallel to each other and the depths of striae were slightly different. As in the photo e_3 and e_4, the hollow patterns due to mechanical force by the bristle of the toothapplication were recognized in the piece with one application with the 1.23% APF solution, and the hollow striae were parallel to each other. At the left and right lower parts of 5000-fold magnification image, the hollow holes suspected of the exposure of the tubules due to mechanical forces were seen.

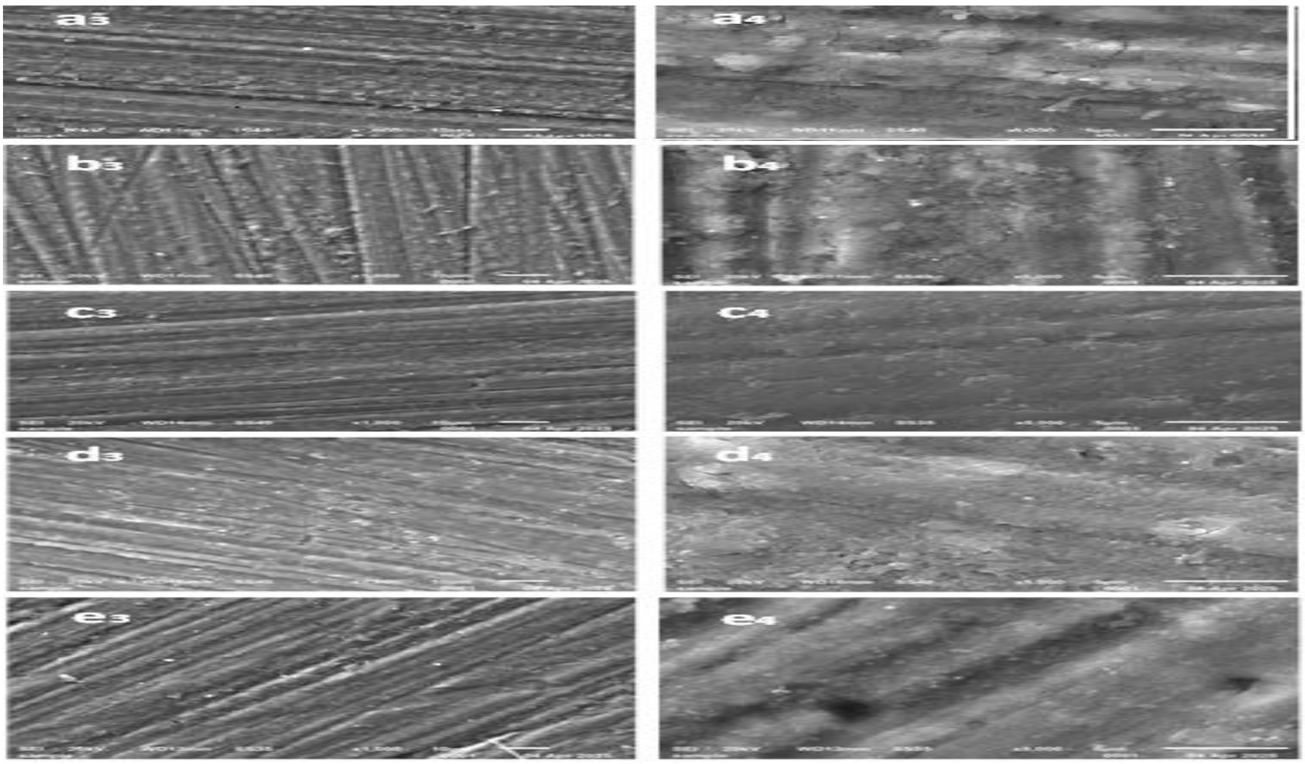

Photo 3. SEM images of fluoride-appied dentin pieces after mechanical stimulation(a_3~e_3; 3000-fold magnification, a_4~e_4; 5000-fold magnification).

a_3: one application with 1.23% NaF-HF solution b_3: two applications with 1.23% NaF-HF solution c_3: three applications with 1.23% NaF-HF solution d_3: one application with 1.23% NaF-HF gel e_3: one application with 1.23% APF solution.

DISCUSSION

Dentin hypersensitivity is a dental irritation that occurs during a meal such as eating or drinking, and is a dental disease with a high prevalence and a serious impact on the quality of life of people. The hydrodynamic theory is the most credible theory among the researches published so far, and the treatment method is to physically close the open dentin tubules. Fluoride is known to react with dental dentin to produce calcium fluoride or fluoroapatite to close dentin tubules to treat hypersensitivity. However, the recurrent disease is common because the formed calcium fluoride or apatite is lost rapidly by mechanical or acidic stimuli [23].

We have focused our attention on the fact that the newly developed NaF-HF gel has high chemical reactivity with dental minerals and the rate of calcium fluoride formation is rapid[24,25] and have researched to investigate the effect of this fluoride on human dental dentin. To date, no studies have investigated the effect of NaF-HF gel on dentin hypersensitivity. Generally, the reaction product between dental enamel and fluoride is calcium fluoride[6], the chemical reactivity of fluoride is evaluated according to its production quantity, and it is considered to be an indicator of the caries preventive effect. We have focused on what the reaction products formed on the surface of human dental dentin were and investigated changes of products and their contents under various conditions. We first have clarified the significance of fluoride formulation and the application number by identifying the reaction products formed on the dentin surface immediately after fluoride application and comparing and evaluating their production quantities. In the control piece, the major mineral was HA, which accounted for 89.99% of the surface of human molar dentin, whereas after the application of fluoride, the major component of the reaction products on the surface of human molar dentin was FA and HA, and the HA content was varied with the change of FA content. Thus, the reaction product was found to be FA. FA content was highest in the pieces with two and three applications with 1.23% NaF-HF solution. FA content in the pieces with one application was in order the piece with one application with 1.23% NaF-HF gel, the piece with one application with 1.23% NaF-HF solution, and the piece with one application with 1.23% APF solution.

This indicates that the application number and formulation of fluoride affect the FA content of dentin pieces. On the other hand, the FA content in the piece with one application with NaF-HF solution was less than that with NaF-HF gel. This means that the gel-like fluoride is more effective than the solution-like fluoride. The high reactivity of the gel is probably because solution is easily washed in water, but the gel penetrates the dentinal tubules and remains on the tooth surface for a certain time and reacts continuously due to the adherence of the gel. Generally, the main reaction product of tooth enamel and fluoride is CaF_2 [24]. However, the fact that the reaction product of dentin and fluoride is FA means that the reaction proceeds differently in two cases. The main component of the inorganic material in enamel is HA, and the organic component is only about 1%. However, there is a slight presence of calcium phosphate, calcium carbonate, etc. with the major inorganic substance, HA in dentin, and about 37% of the organic component, i.e. collagen. Therefore, the reaction form of fluoride with dentin minerals seems to have been different from that of enamel. Thus, as in dental enamel, the reaction product is calcium fluorophosphate, not calcium fluoride. Collagen is a protein that contains NH_3^+ and

COO^- ions at its terminus. The NH_3^+ cation present at the terminus is capable of reacting with the hydroxyl group of hydroxyapatite to form a phosphate-collagen complex. The action of HF with strong oxidative properties on these complexes can break the bonds with protein and combine with phosphate to form fluoroapatite.

In addition, CaF_2 formed in the reaction system can form fluoroapatite by condensation with phosphate present in minerals, especially calcium phosphate. Thus, CaF_2 is the main reaction product for the reaction with hydroxyapatite of enamel, while the main reaction product with dentin is fluoroapatite. In all fluoride-applied pieces(b, c, d, e) as shown in photo b_1~f_1, dentin tubules were not seen and a phase closed by the reaction products with fluoride were seen. However, in the APF-applied piece(f_1), dentinal tubules were not completely closed and the tubule entrance was visible, showing incomplete closure compared to other pieces. We examined the reaction products by XRD and SEM analysis of the pieces after applying fluorides and immersing for 28 days in artificial saliva without washing and the pieces after giving acidic and mechanical stimulation to investigate how reaction products on the fluoride-applied dentin surface of human molar change under the same conditions as the oral environment. After applying fluorides and immersing for 28 days in artificial saliva, the main reaction product on the surface of human molar dentin was ApF and its content varied according to types of pieces. The ApF content was high in the order 3 applications, 2 applications with 1.23% NaF-HF solution, 1 application with 1.23% NaF-HF gel, 1 application with 1.23% NaF-HF solution and 1 application with 1.23% APF solution, but there was no significant difference with the content immediately after reaction(Table 1). However, after acid treatment, as shown in Table 3, the FA contents of all pieces increased than contents after immersion for 28 days in artificial saliva. In addition, in the SEM images, dentinal tubules with circular or elliptical fine entrances completely exposed to the dentin surface of the control group were observed, whereas the tubule entrance in the fluoride-applied pieces was significantly smaller than that of the control group. The sizes of entrances increased in order dentin pieces with 3 and 2 applicationss with 1.23% NaF-HF solution, dentin pieces with 1 application with 1.23% NaF-HF gel, dentin pieces with 1 application with 1.23% NaF-HF solution, and dentin pieces with 1 application with 1.23% APF solution. The formation of micro-holes, despite the increase in the fluorapatite content after acid stimulation, indicates that the absolute fluorapatite content and the resistance to acid attack are not in a propotional relation. In our opinion, dental dentin consists mostly of inorganic materials, especially calcium hydroxide, which is a basic compound, it is readily degraded by the acid-base neutralization reaction when acid applies with it. In addition, if organic acids such as 6% citric acid are continuously applied, calcium fluoride phosphate is also thought to undergo degradation. However, calcium fluoride has a strong acid resistance, so that little decomposition will occur. In addition, calcium fluoride is also decomposed by the action of acid ions, although small amoun of hydrofluoric acid ts is produced, which can react with calcium hydroxide to form calcium fluoride. The chemical reactions for the processes are following:

$Ca_{10}(PO_4)_6(OH)_2$+H^-=Ca^{2+}+PO_4^{3-}+H_2O 1)

$Ca_{10}(PO_4)_6F_2$+2H^-= Ca^{2+}+PO_4^{3-}+2HF 2)

$Ca_{10}(PO_4)_6(OH)_2$+2FH= $Ca_{10}(PO_4)_6F_2$ 3)

By such a mechanism, the content of fluorapatite after the application of organic acids increased than content immediately after the reaction with fluoride shown in Table 2 and content after immersion for 28 days in artificial saliva and giving acidic stimulation shown in Table 3. According to the above mechanism, as in the control group in SEM images, the tubules were partially open, not completely, or were open, but the precipitate was present in it, which was thought to be calcium fluoride, and a small hole was present in the center. The main reaction product on the mechanical stimulation-giving human molar dentin surface was also FA. As shown in Table 8, after mechanical stimulation, the FA content formed on the dentin surface decreased more than that immediately after the reaction in all fluoride-treated pieces. This phenomenon is suspected to be due to the weight loss of dentin by mechanical wear of the bristle on the dentin surface of the toothapplication. In the SEM images of all pieces, the surfaces of the dentin pieces by mechanical stimulation of the toothapplication bristle showed hollow patterns, striae were parallel to each other and the depths of striae were slightly different. Dentin pieces with a single application with 1.23% APF solution showed a hollow pattern by mechanical force due to the bristle of the toothapplication, and the striae was parallel to each other, hollow holes by mechanical force suspected of tubule exposure were seen at the left and right lower sides of the 5000 magnification image. In general, FA is known to have poor mechanical properties, but mechanical resistance in all pieces is probably due to the formation of FA in collagen phase or due to the chemical bonding of the above-mentioned FA with collagen.

The acid stimulation had a greater effect on the size of the hole and the degree of closure of the dentin pieces than mechanical stimulation. Taken together, the above results suggest that acid stimulation has a more negative effect on dentinal tubule closure by fluorapatite formed after fluoride application than mechanical stimulation. However, the chances that organic acids such as 6% citric acid contact with dentin are extremely rare in human daily life and effect of acid is very small due to neutralization and dilution by saliva when drinking acid drinks, and a long time is required for the release of the closed dentin and the development of hypersensitivity. It has been shown that fluoride should be applied whenever symptoms occur to solve dentin hypersensitivity because closed dentin tubles can be open again by the acidic or mechanical stimilation such as toothapplicationing, as the consumption of acidic drinks such as carbonated drinks, lactic drinks and yogurt increases in the people's diet, although fluoride is applied to the dentin tubules.

CONCLUSION

The main reaction product on fluoride-applied human molar dentin surfaces is fluoride apatite, whose content increases as the number of fluoride applications and content in gel-applied piece is higher than that in the solution-applied piece. When giving acidic or mechanical stimulation after appling fluoride and immersion in artificial saliva for 28 days, the acid stimulation has a greater effect on human molar dentin tubule closure than mechanical stimulation. Further randomized controlled clinical trials on the antihypersensitivity effect of 1.23% of NaF-HF gels are needed.

Declaration of competing interest

The authors declare that they have no conflict of interest.

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