Fluoride Coatings on Orthodontic Wire for Controlled Release of Fluorine Ion

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Abstract: The purpose of this study was to develop a new method of releasing fluorine in a controlled manner for applications in the field of orthodontic Ti-based wire, namely the coating of fluorides on Ti. Thin films of two fluoride compounds, CaF2 and MgF2, were coated on Ti via the electron-beam evaporation method. The fluorine was released rapidly from the as-deposited MgF2 coating within a short period, and then the release rate slowed down. When the MgF2 coating was heat treated, this initial burst effect was decreased, but a significant amount of cracks were generated. On the other hand, in the case of the as-deposited CaF2 coating, fluorine was released linearly for the entire period, without an initial burst. In the heat-treated CaF2 coatings the trend was similarly observed. The linear fluorine release from the CaF2 coatings, even in the as-deposited state, was attributed to the high degree of crystallinity of the coatings. A preliminary cell test showed favorable cell viability on both the fluoride coatings. Given their sustained and controlled fluorine release, these fluoride coatings, particularly CaF2, are suggested to be potentially useful in the field of orthodontic Ti-based wire. © 2005 Wiley Periodicals, Inc. J Biomed Mater Res Part B: Appl Biomater 75B: 200–204, 2005

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INTRODUCTION

Finding a new approach to minimize decalcification is imperative in orthodontic treatment, because enamel demineralization has been demonstrated in vivo around orthodontic brackets after only 1 month.1 According to the in vivo and clinical reports, the fluorine ion is known to prevent decalcification and secondary caries.2 Thus, fluorine ions have been administered at significant levels in orthodontic operations. In most cases, the release of fluorine has been facilitated by altering the bonding materials of the brackets, using such materials as glass ionomer cements and light-cured resin-modified cements.3–6 These orthodontic bonding materials have been shown to release fluorine at a rate that could theoretically inhibit enamel decalcification, and the effective range for the inhibition of enamel demineralization was suggested to be about 0.65 to 1.3 μg/cm²/day.5 However, these bonding materials produced maximum fluoride release over the first 1–2 days and the rate of release then decreased rapidly. The abrupt reduction of fluorine release after the initial period restricts the ability of these materials to inhibit secondary caries, because the amount of fluorine released during the later stages is below the level required for therapeutic effects.4

Therefore, it is essential to develop a new source of fluorine ions, which allows them to be released more efficiently in orthodontic applications.7–9 In this study, the authors developed a method of coating fluoride on orthodontic wire for the purpose of releasing fluorine in a controlled manner over a prolonged period. To the best of our knowledge, this is the first report on the deposition of fluoride coatings on titanium-based metals for use as orthodontic wires.

Based on our preliminary studies, we chose the most promising fluorides, which were likely to release fluorine ions in a controlled manner without exhibiting toxicity. Sodium fluoride (NaF) has extremely high solubility in water and therefore cannot be used as a stable coating layer, while lithium fluoride (LiF) exhibited toxic behavior in the preliminary tests of its cellular responses.5 Therefore, the use of these two fluorides as coating materials was precluded.

In this study, we employed two fluorides, magnesium fluoride (MgF2) and calcium fluoride (CaF2), as the coating materials. The e-beam evaporation method was used to deposit a thin film of the fluorides.10 The fluorine ion released from the coatings was examined and analyzed with regard to their potential use in the field of orthodontic wire.

MATERIALS AND METHODS

Sample Preparation

Square-shaped titanium plates with dimensions of 10 × 10 mm and a thickness of 2 mm were prepared. They were
ground with 1000-grit silicon carbide abrasive paper and polished with 1 μm diamond slurry. These substrates were rinsed ultrasonically in acetone, ethanol, and distilled water for 10 min each. For the coating process using electron-beam evaporation, two targets (MgF₂ and CaF₂) were prepared by sintering them at 1100 and 1200°C, respectively, for 3 h. Prior to evaporating the targets, the surface of the Ti plate was pretreated by Ar⁺ bombardment with an ion-beam at 90 V, 2 A for 30 min, to clean and slightly etch the surface. The fluoride targets were evaporated onto the Ti substrate using an e-beam emission current of 10 mA. Each coating layer was formed with a thickness of about 1 μm, and was then heat treated at 300 or 500°C for 2 h.

The chemical structure and degree of crystallization were analyzed by X-ray diffraction (M18XHF-SRA, MAC Science, Tokyo, Japan). The microstructure and morphology of the coatings were observed by scanning electron microscopy (SEM, JSM-6330F, JEOL, Japan).

Fluorine Release

Each specimen was placed in an individual plastic tube containing 10 mL of deionized-distilled water. All of the test tubes were capped and stored in an incubator at 37°C, and the medium was refreshed every 24 h. The dissolution tests were conducted on two different samples for up to 3 weeks. Ion chromatography (IC, DX-120, DIONEX, USA) was used to detect the amount of fluorine ions released from the coatings. A 0.5-mL sample of each solution was injected into the injection loop of the instrument. The loop was designed such that 250 μL was fed to the column for analysis. Fluorine ions have a well-defined retention time, and the peak corresponding to fluorine was readily determined from the chromatogram. The determination of each solution was performed three times and the fluorine concentration was determined to an accuracy of 0.05 ppm. The concentration of fluorine ions was converted to the amount of fluorine release per unit surface area of the specimen (μg/cm²).

Cell Viability

An in vitro cell test was performed to confirm the cell viability of the fluoride coatings. Human osteosarcoma (HOS) cells were plated on both the fluoride coatings and the Ti metal without the coating (control) at a density of 3 × 10⁴/cm². After incubation at 37°C for 3 days, the cells were detached with trypsin-EDTA solution, and centrifuged at 1300 rpm for 5 min. After staining the dead cells with trypan blue, the number of viable cells was counted using a hemocytometer. Each set of tests was performed in triplicate (n = 3).

RESULTS

MgF₂ Coating

Figure 1 shows the XRD patterns of the MgF₂ coatings on Ti without and with heat treatment at different temperatures. The as-deposited coating showed only Ti substrate peaks, suggesting that the coating layer was in an amorphous state. After heat treatment at 300°C, small MgF₂ peaks were observed, and the peak intensity increased slightly as the heat treatment temperature was increased to 500°C. Furthermore, titanium fluoride peaks were observed, suggesting that a reaction occurred between the coating and the Ti substrate.

CaF₂ Coating

Figure 4 shows the XRD patterns of the CaF₂ coatings on Ti without and with heat treatment at different temperatures. The as-deposited layer showed a uniform and dense morphology, and the grain size of the coating layer was approximately 50 nm [Figure 2(A)]. However, when the layer was heat treated at 300°C, a significant amount of cracks was formed [Figure 2(B)].

The release of fluorine from the MgF₂ coatings was measured by incubating the coatings in distilled water for up to 20 days, as shown in Figure 3. Initially, fluorine was released rapidly from the as-deposited coating, but the rate of release subsequently decreased. After the coating was heat treated, the amount of fluorine released decreased markedly and the initial burst effect was also reduced.

Figure 1. XRD patterns of the MgF₂ coatings on a Ti substrate deposited by the e-beam evaporation method without and with heat treatment.
heat treated at 500°C, the crystals became slightly bigger [Figure 5(B)]. From a cross-section view [Figure 5(C)], the thickness of the as-deposited CaF$_2$ layer was observed to be approximately 1.5 µm. The coating layer was highly dense and uniform, and did not show any cracks or delaminations.

The release profile of fluorine ions from the CaF$_2$ coatings is presented in Figure 6. For all the coatings, with and without heat treatment, the release of fluorine ions was linear over time, and did not exhibit any burst release in the initial stages. The release rate of the as-deposited coating was approximately 1.67 µg/cm$^2$/day. When the CaF$_2$ coating was heat treated at 500°C, the release rate was reduced slightly (1.58 µg/cm$^2$/day), but the linear release pattern was still maintained.

Cell Viability

To observe the cell viability of the fluoride coatings, osteoblastic cells were cultured on the fluoride coatings for 3 days. Figure 7 shows the proliferation level of the cells on the coatings heat treated at 300°C. Cells grew favorably on both the CaF$_2$ and MgF$_2$ coatings. In particular, the cells on the CaF$_2$ coating proliferated at a significantly higher level ($p < 0.05$) with respect to the pure Ti substrate.

**DISCUSSION**

This work constitutes the first feasibility study of the use of fluoride coatings on Ti-based metals for the application in orthodontic wire. Currently, in the orthodontic area, fluorine is administered by using bracket bonding materials. However, these bonding materials typically exhibit an unsatisfactory fluorine ion release pattern, that is, an initial burst release in the first 1–2 days, subsequently followed by an abrupt decrease in the release rate.$^{12-14}$ This release pattern has a limitation in that it fails to elicit the desired fluorine effects efficiently. The small but frequent and prolonged release of fluorine ions is regarded more effective clinically.$^{15}$
The MgF$_2$ coatings, introduced as a possible alternative fluoride coating on Ti, showed an initial rapid release of fluorine ions, especially in the case of the as-deposited coating. This was attributed to the poor crystallinity of the MgF$_2$ layer. Although after heat treatment, the crystallinity was improved and the initial burst effect was reduced, the generation of cracks due to thermal mismatch constituted a major shortcoming of this material. Consequently, this problem needs to be solved before MgF$_2$ can be considered for real applications.

Of special note is the fact that the CaF$_2$ coatings did not show this initial rapid release, in contrast to the commercial orthodontic bonding materials$^{17-19}$ and MgF$_2$ coatings. Rather, the release rate was almost constant during the entire test period. Such a linear release pattern is the objective of controlled release systems, because it allows the exact amount of material released to be easily predicted. The calculated fluorine release rates from the CaF$_2$ coatings were in the approximate range of 1.58–1.67 $\mu$g/cm$^2$/day depending on the heat treatment temperature, and this level is considered to prevent the formation of secondary caries effectively, given that the recommended rate of release from the bonding material is about 0.65–1.3 $\mu$g/cm$^2$/day.$^5,15$

The fact that the as-deposited CaF$_2$ coating exhibited a linear profile, similar to that observed for the heat-treated coatings, is of particular note. This is attributed to the high crystallinity of the CaF$_2$ coating, even in the as-deposited state.
state. Normally, the coatings deposited by e-beam deposition need subsequent heat treatment, to crystallize the coating structures. However in this CaF₂ system, the crystallinity of the as-deposited layer was particularly high. This method of synthesis, without the requirement for the heat treatment step, is beneficial in that it allows the metallic wire to be manipulated safely and the fabrication cost to be lowered.

Another benefit of the fluoride coatings lies in the form of fluorine released. In the ion chromatography data, only the free fluorine ion was detected without the presence of any complex forms, which is in contrast to the resin-based orthodontic materials where the fluoride was also released in the form of complexes.20–22 Only the free fluorine ions are known to be effective in imparting resistance to secondary caries, because they can be taken up easily into the tooth structure and transform hydroxyapatite into fluorapatite.23

From the preliminary cell viability test, it was concluded that both the CaF₂ and MgF₂ coatings exhibited favorable cell responses, and this should rule out the concerns about its toxicity in real applications. Based on these findings, the fluoride coatings on Ti described in this study, particularly the CaF₂ coating, are strongly recommended for use in the orthodontic area. A more detailed study of these fluoride coatings is underway for the purpose of optimizing the thickness and composition of the coating layer, to tailor the release amount and period of fluorine ions. Furthermore, the investigation of the mechanical stability of the coatings and of the fluorine release from the coating on the commercial orthodontic wire remain as further study.

CONCLUSION

The fluoride coatings of CaF₂ and MgF₂ were deposited via e-beam evaporation to release fluorine in a controlled manner in orthodontic applications. The release of fluorine ions from the MgF₂ coating exhibited an initial burst, subsequently followed by a reduced release rate. Although the initial burst effect was reduced with heat treatment, severe cracks were formed on the surface. In contrast, the CaF₂ coating did not exhibit the initial burst effect in the as-deposited state, but showed a linear release profile over the entire test period. This linear release of fluorine was attributed to the high degree of crystallization of CaF₂, even in the as-deposited state. This linear release of fluorine, along with the favorable cell viability, makes the CaF₂ coating a potential candidate material for fluorine releasing orthodontic wire.

REFERENCES