Coating NiTi archwires with diamond-like carbon films: reducing fluoride-induced corrosion and improving frictional properties

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Coating NiTi archwires with diamond-like carbon films: reducing fluoride-induced corrosion and improving frictional properties

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Abstract This study aims to coat diamond-like carbon (DLC) films onto nickel–titanium (NiTi) orthodontic archwires. The film protects against fluoride-induced corrosion and will improve orthodontic friction. 'Mirror-confinement-type electron cyclotron resonance plasma sputtering' was utilized to deposit DLC films onto NiTi archwires. The influence of a fluoride-containing environment on the surface topography and the friction force between the brackets and archwires were investigated. The results confirmed the superior nature of the DLC coating, with less surface roughness variation for DLC-coated archwires after immersion in a high fluoride ion environment. Friction tests also showed that applying a DLC coating significantly decreased the fretting wear and the coefficient of friction, both in ambient air and artificial saliva. Thus, DLC coatings are recommended to reduce fluoride-induced corrosion and improve orthodontic friction.

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1 Introduction

Nickel–titanium (NiTi) archwires have been applied in orthodontic treatment for several decades because of their effective biocompatibility and super-elasticity [1–3]. The super-elasticity of NiTi archwires facilitates periodontium remodeling by producing a continuous light force. However, they are still controversial for long-term clinical applications because they reduce corrosion resistance in active saliva or fluoride solutions [4, 5]. Mouthwash that contains fluoride can dissolve the protective TiO_2 surface layer [6] and are commonly used to prevent dental caries and decalcification. Ni ions, which can cause adverse reactions such as anaphylaxis and intoxication, can be released through corrosion processes [7]. Furthermore, NiTi archwires are known for 'high friction coefficient relativity' [8]. The superficial corrosion of archwires may lead to an increase in surface roughness. These adverse effects decrease tooth movement and it is difficult to optimize NiTi archwires for use in orthodontic applications.

To improve long-term biocompatibility and frictional characteristics, various surface modification methods have been applied to orthodontic appliances [9–12]. Diamond-like carbon (DLC) films are promising contributions for this bioapplication, owing to their low friction coefficient, chemical inertness and high corrosion resistance [13]. In recent studies, DLC films are widely expected to be adapted as a new biocompatible coating to reduce nickel release from NiTi alloy archwires [14]. However, this technique has not yet been sufficiently applied in the field of dentistry, especially for orthodontics. Until now, DLC films have not been used as coatings to protect NiTi archwires against corrosion in fluoride-containing oral environments.

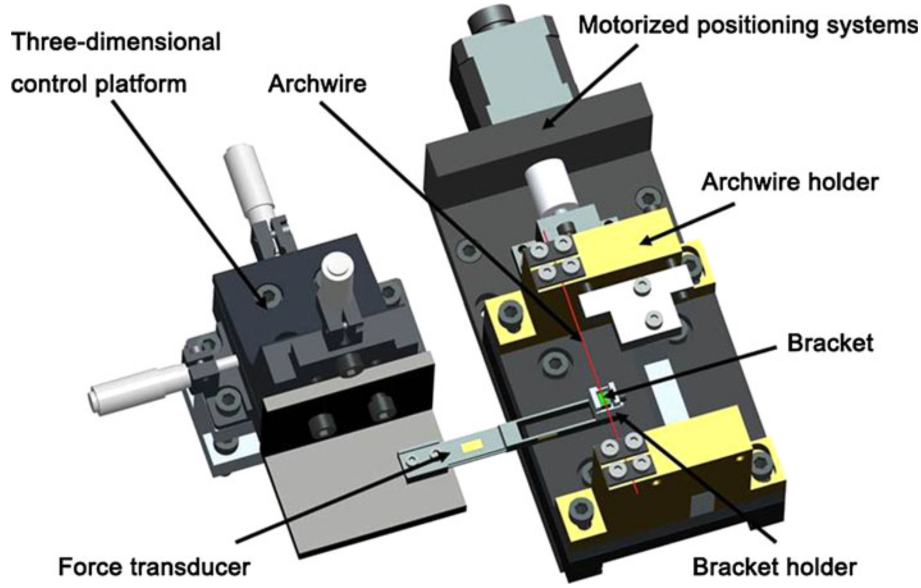

Fig. 1 Scheme of the orthodontic fretting test equipment

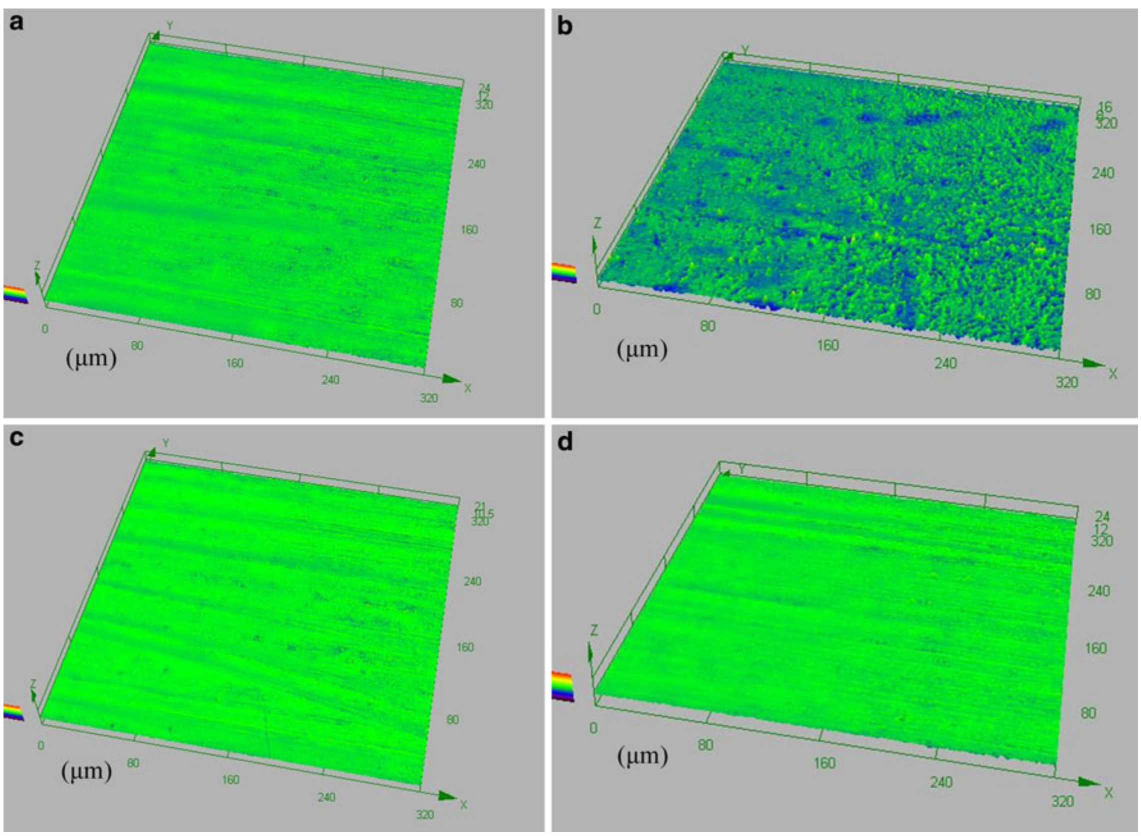

Fig. 2 Surface analysis of NiTi archwires by 3D measuring laser microscope. **a** Uncoated wire before fluoride immersion. **b** Uncoated wire after fluoride immersion. **c** DLC-coated wire before fluoride immersion. **d** DLC-coated wire after fluoride immersion

In this study, DLC films were deposited by 'mirror-confinement-type electron cyclotron resonance (MCECR) plasma sputtering' on nickel-titanium orthodontic wires. The effects of the DLC coating on fluoride-induced corrosion and friction behavior of the archwires were assessed.

2 Materials and methods

2.1 Preparation of samples

Orthodontic NiTi archwires, with a rectangular cross-section of 0.019 in. × 0.025 in. (0.48 mm × 0.64 mm), (commercially available from Grikin Advanced Materials Co., Ltd., Beijing, China), were used in this study. The wires were ultrasonically cleaned with acetone, absolute ethanol and de-ionized water, each solution used separately for 5 min. Wires were fixed with custom-made jigs in the vacuum chamber of MCECR equipment [15]. Carbon films were deposited on both sides of the wire under the same conditions. Deposition was carried out at a base pressure of 2×10^{-4} Pa and a deposited pressure of 2×10^{-2} Pa. The discharge gas used was argon. The substrate was kept at a bias voltage of +60 V and the maximum temperature was approximately 90 °C. In our preliminary study, the deposition rate has been calculated from the film thickness and deposition time. The thickness of the DLC film was controlled by changing the ion sputtering time. In the present study the deposited time was 25 min, and the film thickness was approximately 100 nm.

2.2 Immersion test

The purpose of this test was to evaluate DLC-coated archwires for fluoride-induced corrosion protection. Ten coated and uncoated archwire specimens were chosen for the immersion test. A 20 mm length segment was cut from each archwire. Specimens were cleaned and de-greased for 5 min in acetone, and then immersed in 'high fluoride ion concentration mouth rinse'. This immersion mimicked the use of a fluoride mouth rinse as described by Krishnan et al. [16]. Each specimen was dipped into a Phos-Flur anticavity dental rinse containing sodium fluoride in acidulated phosphate solution, 0.044 % sodium fluoride (0.02 % fluoride ion) with 0.1 M phosphate, pH 4, (Colgate Oral Pharmaceuticals, Inc., New York, USA), in a 15 ml polypropylene (PP) tube, at 37 °C. An immersion cycle of 5 min, three times a day, was conducted for 12 weeks. During the remainder of the time the specimens were immersed in artificial saliva (0.900 g/l NaCl, 1.200 g/l KCl, 0.052 g/l $MgCl_2$, 0.530 g/l Na_2HPO_3, 0.038 g/l Na_3PO_3, 0.330 g/l methylparaben, 10.000 g/l polyvinyl alcohol, 30 ml/l glycerin).

Before and after the immersion test, the surface topography of the archwires was evaluated using a 3D measuring laser microscope (Olympus Lext OLS4000, Olympus Europa Holding GmbH, Hamburg, Germany) during which the surface roughness was also measured. The roughness (R_a) was calculated by software that was supplied with the 3D measuring laser microscope at five different areas for each archwire. The mean value of the measurements was used.

Statistical analysis was performed using the SPSS version 14.0 statistical package. The mean values of the surface roughness, before and after the immersion test, were statistically analyzed using a paired-sample t test ($P < 0.05$).

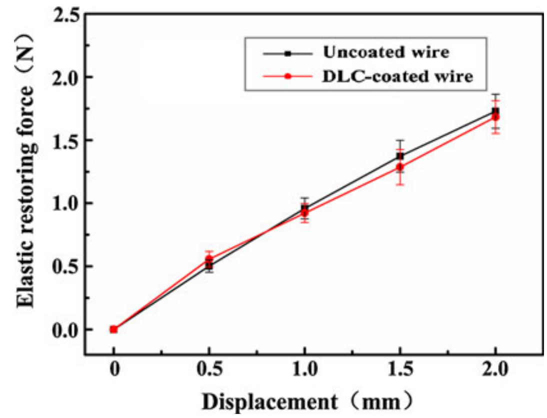

Fig. 3 Representative load–deflection curve of DLC-coated and uncoated wires

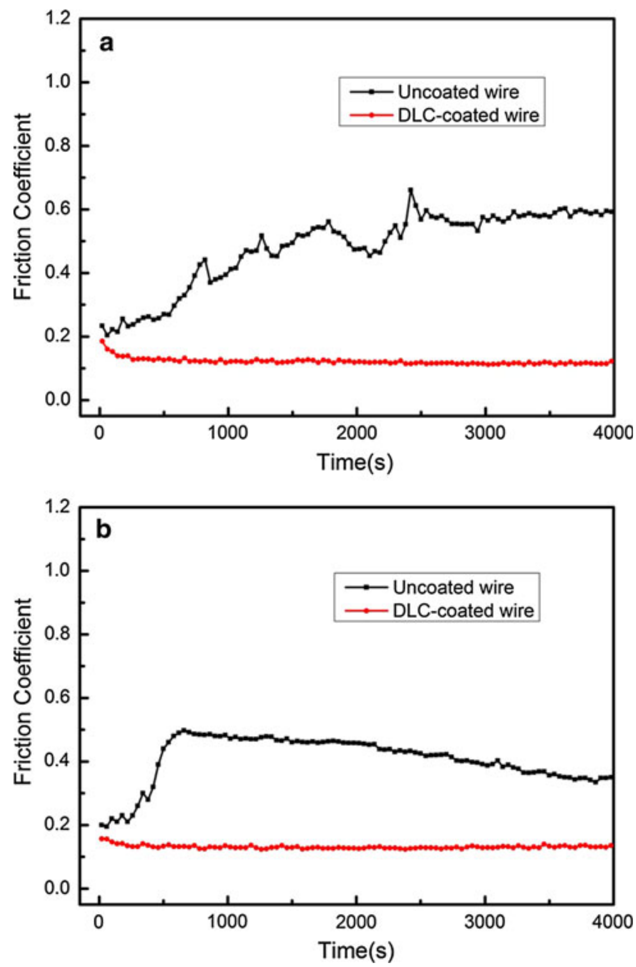

Fig. 4 Friction evaluation of the studied tribo-couples in **a** ambient air and **b** artificial saliva

2.3 Load deflection test

The load deflection characteristics of the archwire specimens were tested using specially designed experimental

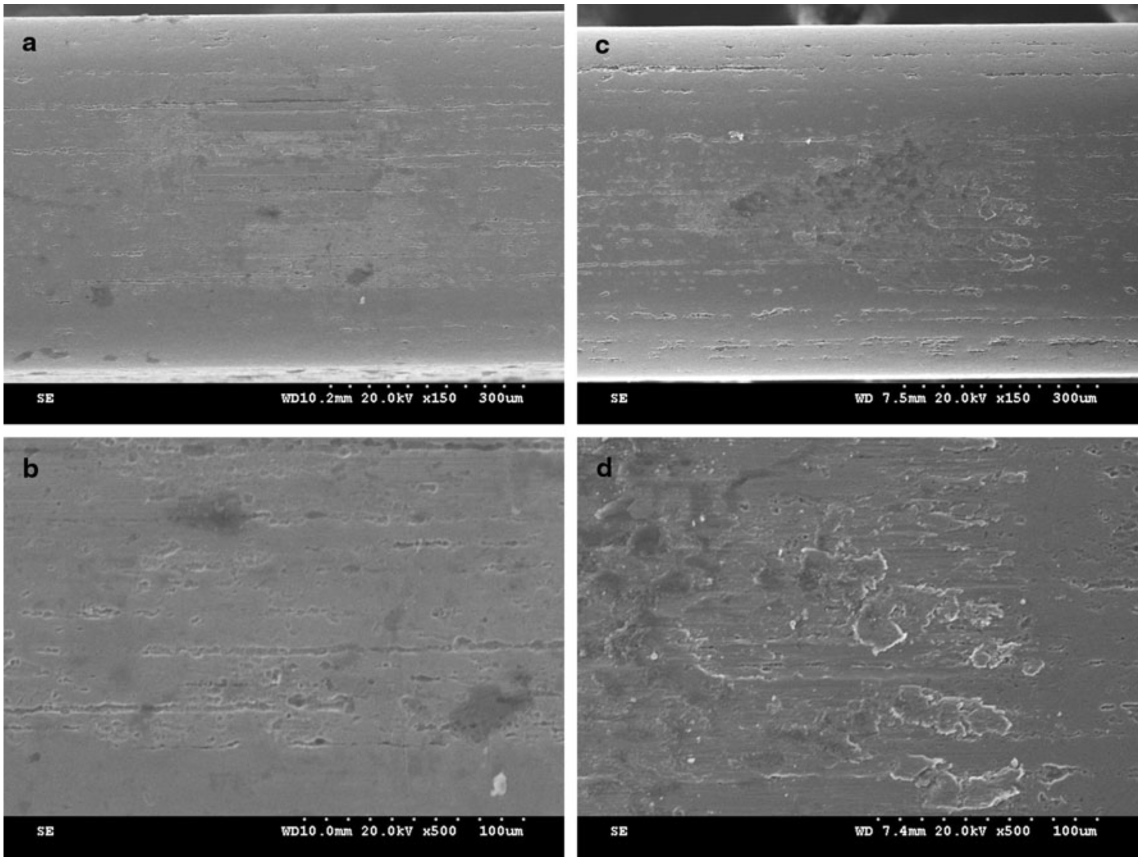

Fig. 5 SEM images of the fretting scars on archwires after testing in ambient air (×150, ×500 magnification). **a**, **b** DLC-coated wire; **c**, **d** uncoated wire

equipment (Fig. 1). The straight segments of the preformed wires were placed on the 0.64 mm side and the distance between the two supporting contacts was fixed at 10.0 mm. Each specimen was loaded to 2.0 mm and then unloaded to zero deflection at a crosshead speed of 1 mm per minute. The elastic restoring force was recorded at deflections of 0.5, 1.0, 1.5 and 2.0 mm. Measurements were made only during loading, not during unloading, of the specimen. All wires were tested five times. The load value was obtained after each test run to be tabulated and statistically analyzed.

2.4 Friction test

By sliding the coated and uncoated archwires through the bracket slot, the friction coefficient at the orthodontic bracket-wire interface was determined. Stainless steel brackets (3M Unitek, 3M Company, Monrovia, California) with slot sizes of 0.022 in. (0.56 mm) were used. All the tests were carried out using a specially designed fretting test system, consisting of reciprocating tangential displacements [17]. Samples were fixed onto specific holders designed for this purpose. The archwires were attached to the moving part. The brackets were stuck and fixed onto the bottom holder connected to the sensor using resin (Fig. 1). Before mounting the holders, the couples to be tested were cleaned and de-greased for 5 min in acetone. A 1 N normal force was kept constant. Similar loading conditions had been imposed for all studied tribo-couples. Tests were run with ±150 μm displacement amplitude at a frequency of 0.5 Hz. The amplitude, velocity and number of such fretting cycles could be pre-set. With these settings, no obvious macro-sliding could be seen. The measurements were conducted under ambient air (room temperature of 25 °C) and an artificial saliva environment. A peristaltic pump provided continuous artificial saliva, maintaining a constant temperature (37 °C), which simulated the oral environment.

After the fretting test had been carried out, the surface morphology of the archwires was evaluated with a scanning electron microscope (Hitachi, S-3000N, Hitachi Science Systems, Ltd., Japan). Specimens were observed at various magnifications (150–500 times) and representative micrographs were acquired. The images allowed us to assess the micromorphologic characteristics of the wear surfaces.

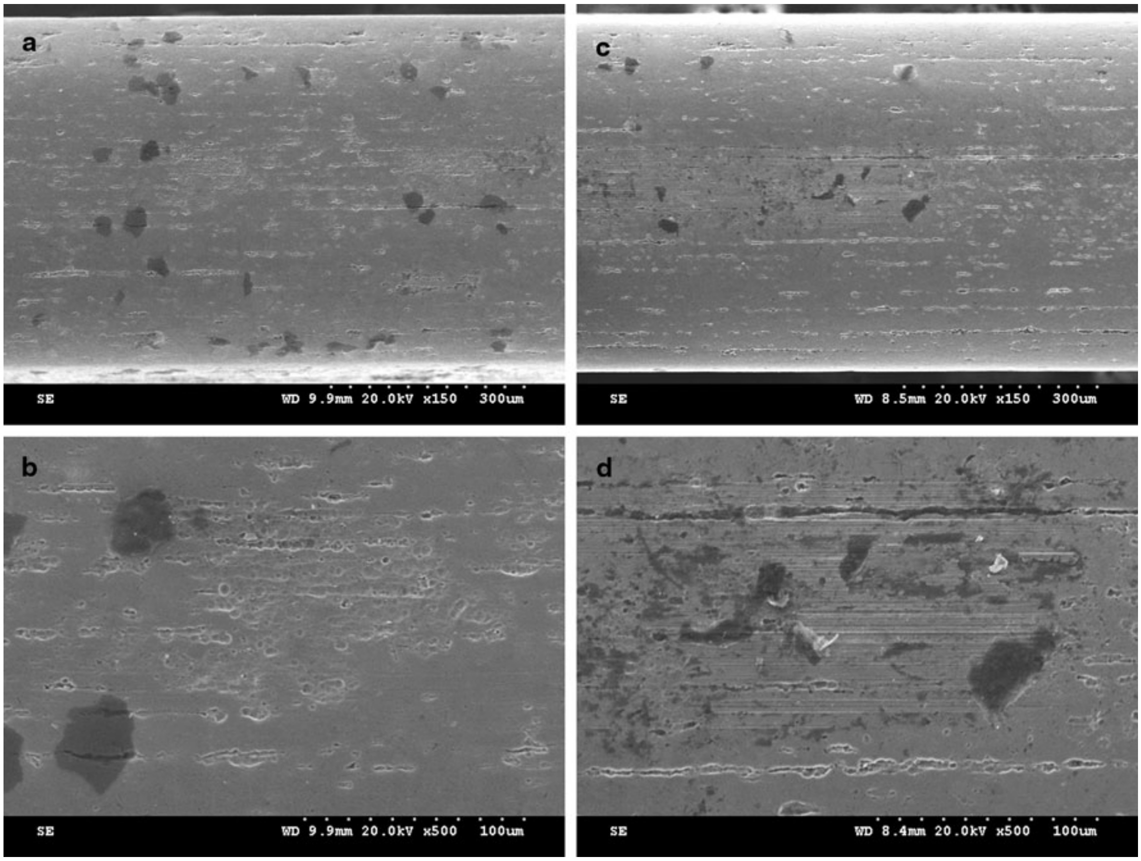

Fig. 6 SEM images of the fretting scars on archwires after testing in artificial saliva (×150, ×500 magnification). **a**, **b** DLC-coated wire; **c**, **d** uncoated wire

3 Results and discussion

As the 3D visualization showed, the uncoated and DLC-coated archwires had similar surface morphology. The surface roughness of the coated archwires was not significantly low compared with the uncoated archwires (Fig. 2a, c).

The uncoated archwires revealed a dimpled and cracked surface texture when they were subjected to fluoride attack (Fig. 2b). There was further increase in roughness (before immersion: $R_a = 0.291$ μm and after immersion: $R_a = 0.566$ μm) after the immersion test. Statistical evaluation revealed significant differences before and after the immersion test for uncoated archwires. However, the DLC-coated archwires were found to be superior, with no obvious change to the surface after fluoride immersion. There was only a slight increase in this roughness (before immersion: $R_a = 0.283$ μm; after immersion: $R_a = 0.307$ μm), which was statistically insignificant. The results further emphasize the fact that the DLC coating is less affected by corrosion [10], and indicates the favorable effect of DLC films in protecting against fluoride-induced corrosion.

The representative load–deflection curves of DLC-coated and uncoated wire samples are shown in Fig. 3. Statistical analysis revealed no significant difference between the elastic restoring force of DLC-coated and uncoated wires. This indicated that the DLC coating did not influence the free super-elastic property of the NiTi archwires. Such behavior could be related to the coating thickness. The mean values for the coating thickness, obtained over substrate wires, were only 100 nm. The film coatings were too thin to affect the surface topography and to restrict the free super-elastic deformation of the NiTi alloy core.

The average friction coefficient of the uncoated archwires and the DLC-coated archwires, as a function of fretting time, is shown in Fig. 4. In ambient air, an increasing curve of the friction coefficient for uncoated archwires was observed. The maximum and stable values of the friction coefficient were approximately $\mu_{max} = 0.68$ (after 2,400 fretting seconds) and $\mu_{stab} = 0.59$ (after 3,000 fretting seconds), respectively. Meanwhile, after an initial sharp decrease of friction coefficient, DLC-coated archwires reached stable friction behavior. The lower friction coefficient was observed for the DLC-coated archwires with $\mu_{max} = 0.18$ (at the beginning of fretting) and approximately $\mu_{stab} = 0.12$ (after 100 fretting seconds).

In the artificial saliva environment, the initial friction coefficient for uncoated archwires sharply increased up to its maximum (after approximately 700 fretting seconds).

The friction coefficient then decreased smoothly. Similarly, the higher friction coefficient was observed with the corresponding values $\mu_{max} = 0.50$ and $\mu_{stab} = 0.40$. The tendency is similar to the frictional behavior in ambient air for DLC-coated archwires, and the maximum and stable values of the friction coefficient were approximately $\mu_{max} = 0.16$ and $\mu_{stab} = 0.12$.

The results confirm good frictional characteristics of the DLC coatings [13]. The improvement in the wire-bracket friction is especially favorable for the early alignment stages of orthodontic therapy because of its high slip capacity, which will allow for greater efficiency of tooth movement. The friction tests also indicate that the saliva medium tends to decrease the friction coefficient for the uncoated wires by allowing for lubrication of the interface [18]. However, this does not affect the friction coefficient for the DLC-coated tribo-couples under test conditions. Although further research should be conducted to explain such tendencies, we may conclude that DLC-coated archwires display superior friction properties in orthodontic applications.

The surface change on the archwires, after friction testing, is shown in Figs. 5 and 6. Surface modifications with extensive signs of wear, were seen on the surfaces of the uncoated archwires when compared with the DLC-coated archwires. Micrographs indicated that low wear took place for the DLC-coated surfaces, regardless of the ambient conditions. DLC thin film coatings were found to be relatively stable in the friction test. In orthodontic treatments, the application of DLC coating can improve the frictional properties at the contact interface between the archwire and bracket because of its low wear and low friction coefficient.

4 Conclusions

The influence of DLC films on the fluoride-induced corrosion resistance and frictional performance of NiTi archwires has been investigated. The results of the immersion tests showed that surface roughness variations on the archwires, caused by fluoride-induced corrosion, were reduced by 91.3 % due to the protection of the DLC films. The friction test results revealed that the friction coefficient of the DLC-coated tribo-couple was significantly reduced by up to 79.7 % in ambient air and 70.0 % in artificial saliva, compared with the uncoated ones. The results indicate that DLC films not only increase the corrosion resistance of NiTi archwires, but also significantly improve their frictional properties, showing that DLC films have great potential in orthodontic applications.

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