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Investigation of Diamond-Like Carbon Coating for Orthodontic Archwire

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A diamond-like carbon (DLC) film-coated nickel-titanium (Ni-Ti) orthodontic archwire was fabricated by an arc-discharge ion-plating process. The purpose of such a coating was to prevent Ni ion release and the toxic effects of the Ni-Ti archwire. The stability of the DLC film coating during the brushing of teeth and its effect on Ni ion release were investigated. The surface morphology of the DLC/Ni-Ti archwire and the amount of Ni ion released were determined by scanning electron microscopy (SEM) and microwave-induced plasma mass spectroscopy (MIP-MS), respectively. The SEM images show that there was no significant damage such as cracking or corrosion of the DLC film at the archwire surfaces. In the immersion test, the amount of Ni ion release was reduced by 80% using a DLC film coating. In addition, the relationship between cytotoxicity and DLC film coating was investigated. The DLC film coating inhibited the effect of the Ni-Ti archwire on cell growth. Accordingly, the DLC film coating is expected to provide multiple improvements to the properties of Ni-Ti archwires, and is applicable to dental materials to improve the stability of orthodontic archwires.

1. Introduction

Amorphous hydrogenated carbon films have attracted considerable interest in many industrial fields. In particular, diamond-like carbon (DLC) films have attractive characteristics, which include their resistance to prevent corrosion against chemicals (acid and alkaline solutions), high electrical resistance, extreme hardness, low friction,

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high thermal conductivity, and biocompatibility.(1–5) The combination of these properties enables many practical applications of DLC film coatings. In the early 1990s, Grill suggested that DLC film coatings are excellent biomaterials for protecting implants and helping them accomplish their function.(1) Biomaterials that are implanted in the human body can interact with cells and fluids, and are subjected to corrosion from organic materials in the body. The interactions of these implants with body cells, the products of the induced corrosion, and the debris from wear can have an adverse effects on the body and on the implants. These effects include cellular damage, infections, blood coagulation, and the failure of the implants. In a large number of reports, researchers have discussed the biomedical applications of DLC film coatings, *e.g.*, in hip and knee joints, artificial heart valves and diaphragms of artificial heart blood pumps, coronary stents, and contact lenses.(1–3,6) However, research on the application of DLC films as dental and/or orthodontic devices has not been sufficient.

One of the biomaterials, nickel-titanium (Ni-Ti) alloy, which has attracted considerable interest as a shape memory alloy and for its superelasticity, has been used in implants of orthopedic and orthodontic devices as self-expanding stents and graft support systems.(7–12) However, in *in vivo* studies on the use of Ni-Ti in orthodontic devices, several cases of severe inflammatory reactions resulting in contact dermatitis and oral lesions have been reported.(7,13) It was found that corrosion of the Ni-Ti orthodontic archwire led to nickel (Ni) ion release.(7–9,14,15) This could have resulted in an accumulation of Ni ions in the recipient's body, and this would have manifested itself as toxic effects. Therefore, the suppression of corrosion and increased wear resistance of Ni-Ti orthodontic archwires are desirable.

In this study, a DLC-film-coated Ni-Ti orthodontic archwire (DLC/Ni-Ti archwire) was fabricated to prevent Ni ion release and the toxic effects of the Ni-Ti archwire. DLC films have attractive properties including their resistance to corrosion by acid and alkaline solutions;(1–5) thus, the DLC film coating is expected to inhibit Ni ion release and provide multiple improvements to the properties of Ni-Ti archwires. We investigated the stability of the DLC film coating during the brushing of teeth and its effect on Ni ion release. In addition, the relationship between cytotoxicity and DLC film coating was investigated.

2. Materials and Methods

2.1. *Deposition of DLC film on Ni-Ti alloy orthodontic archwires and brushing test*

A DLC film was deposited on a Ni-Ti archwire by arc-discharge ion-plating. A schematic diagram of the deposition system (Model: DASH 860, Nanotec Co., Saitama, Japan) is shown in Fig. 1. The DLC film was deposited on Ni-Ti archwires (Model: TMSJ-09, Tomy International Inc., Tokyo, Japan). The arc-discharge plasma decomposed benzene (C_6H_6: 99.9999%), which was the source gas. In this study, the film thickness was controlled to approximately 1 μm under the following deposition conditions: gas pressure = 2.3×10^{-5} Pa, deposition time = 3.5 h, and substrate bias voltage = –2.0 kV. The characteristics of the DLC film deposited on the Ni-Ti archwire

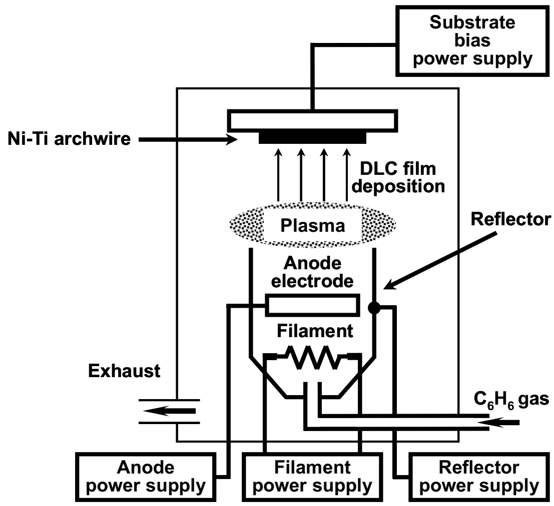

Fig. 1. Schematic diagram of arc-discharge ion-plating system for DLC film deposition on an orthodontic archwire.

were analyzed using an argon-laser Raman spectrophotometer (Model: NRS-2100, JASCO Co., Tokyo, Japan). After the DLC film deposition, the stability of the DLC film coated on the orthodontic archwire was investigated using a mechanical brushing machine with a toothbrush (Model: K654, Tokyo Giken Ltd., Japan). A schematic diagram of the system is shown in Fig. 2. The brushing test was carried out for 250 min at a constant load of 3.25 N. The frequency of the brushing is 100 times per min. This experiment was estimated to be equivalent to daily brushing for six months. Before and after the brushing test, the surface morphology of the DLC/Ni-Ti archwire was observed by scanning electron microscopy (SEM, Model: JSM-5310LVB, JEOL Ltd., Tokyo, Japan).

2.2. *Immersion tests and nickel ion release from Ni-Ti alloy archwires*

The system used for the immersion test is shown in Fig. 3. To obtain a marked Ni ion release over a short period, the experimental conditions were selected as follows; three DLC/Ni-Ti and Ni-Ti archwires were each fully immersed in 7 ml of a physiological saline solution (Otsuka Pharmaceutical Co., Ltd., Tokyo, Japan) maintained at 85°C for five days. Secondly, to estimate the Ni ion release over a long-term period under physiological conditions, the immersion test was carried out for six months at a constant temperature of 37°C.

After the immersion tests, the concentration of Ni ions in the physiological saline solution derived from the Ni-Ti alloy archwires was measured by microwave-induced plasma mass spectroscopy (MIP-MS, Model P-6000, Hitachi, Ltd., Tokyo, Japan). Before and after the immersion test, the surface morphologies of the DLC/Ni-Ti and Ni-Ti archwires were observed by SEM.

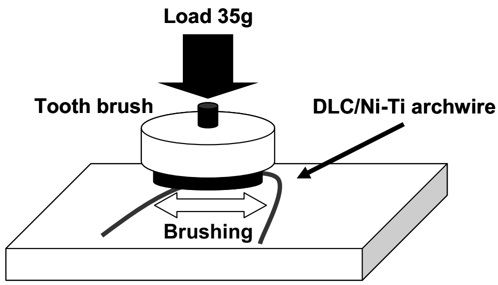

Fig. 2. Schematic diagram of the mechanical brushing test, which was carried out for 250 min at a constant load of 3.25 N. The frequency of the brushing is 100 times per min.

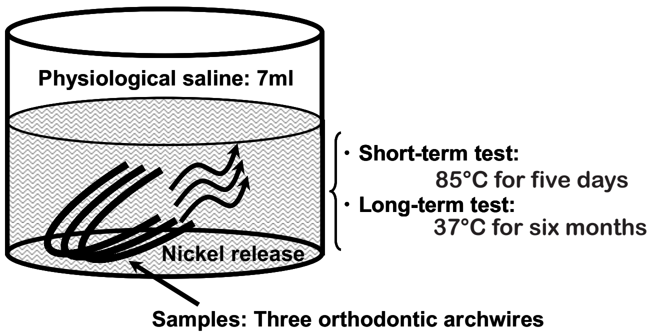

Fig. 3. Immersion test system used for determining "Ni ion release rate" from DLC/Ni-Ti and Ni-Ti archwires. Three archwires of DLC/Ni-Ti and Ni-Ti were fully immersed in 7 ml of physiological saline.

2.3. *Relationship between DLC film coating and cell growth*

In this experiment, a squamous cell carcinoma derived from human oral cancer (Sa3, Model RCB0980, Riken, BioResource Center, Ibaraki, Japan) was used for the cell culture. The Sa3 cells were seeded in each well of a 24-multiwell insert system (Falcon 353047, Becton, Dickinson and Co., New Jersey, USA), and prepared in an Eagle's Minimum Essential Medium (E-MEM) solution and adjusted to a density of 2×10^4 cells/ml. The amount of E-MEM in each well was 1 ml. After incubation at 37°C, (employing the same conditions as the cell preparation process) for 24 h, DLC/Ni-Ti and Ni-Ti archwires, which were cut to 10 mm, were immersed in the each well containing the seeded Sa3 cells. The system used for the cell culture experiment is shown in Fig. 4. The control did not contain any archwires. The Sa3 cells were then cultured in the E-MEM containing the archwires for four days. The number of cells was determined using a Neubauer hemacytometer (Model A116, Sun Lead Glass Co., Ltd., Tokyo, Japan).

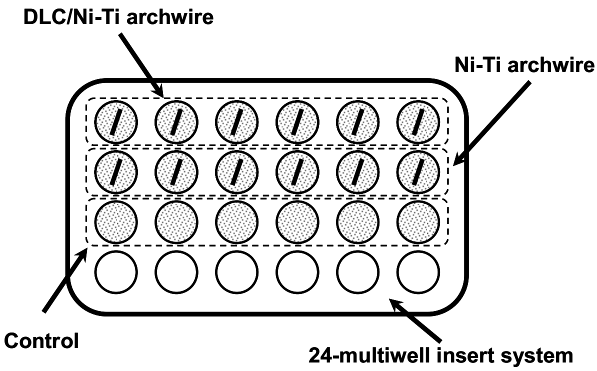

Fig. 4. System used for cell culture experiment. DLC/Ni-Ti and Ni-Ti archwires, which were cut to 10 mm, were immersed in each well containing the seeded Sa3 cells (2×10^4 cells/ml). The control did not contain any archwires.

3. Results and Discussion

3.1. *Deposition of DLC film on Ni-Ti alloy orthodontic archwires and brushing test*

The Raman spectra of DLC/Ni-Ti and Ni-Ti archwires are shown in Fig. 5. The DLC/Ni-Ti archwire exhibited two broad Raman peaks at 1330 and 1560 cm^{-1}. The Raman spectra of disordered graphite show two distinct peaks, a *G*-peak around 1540–1580 cm^{-1} and a *D*-peak around 1350 cm^{-1}; the *G*-peak is assigned to the E_{2g} symmetric vibration mode of graphite layers in the microdomain of DLC films.(16) The relative intensities of the *D*- and *G*-peaks strongly depend on the characteristics of the DLC film. In this experiment, it was observed that the spectrum of the DLC film was similar to that of a typical DLC film. On the other hand, in the Raman spectrum of the Ni-Ti archwire, no signal was observed around the *D*- and *G*-peaks. From the results of the Raman analysis, it is clear that the DLC film was deposited successfully on the Ni-Ti alloy orthodontic archwires.

To investigate the stability of the DLC film during the brushing test, we observed SEM images of the surface morphology of the DLC/Ni-Ti archwire before and after the brushing test. The SEM images show there was no significant damage such as peeling or cracking of the DLC film at the surface during the brushing test. The stability of the DLC film was sufficient for the brushing of teeth.

3.2. *Immersion tests and nickel ion release from the Ni-Ti alloy archwires*

The immersion tests were carried out to test the archwires in physiological saline at 85°C for five days and at 37°C for six months. It was shown by the SEM images that the surface of the DLC film coating suffered no corrosion in the immersion tests. This means that the surface of the DLC/Ni-Ti archwire was highly stable in the immersion test. Figure 6 shows SEM images of the surface of the Ni-Ti and DLC/Ni-Ti archwires

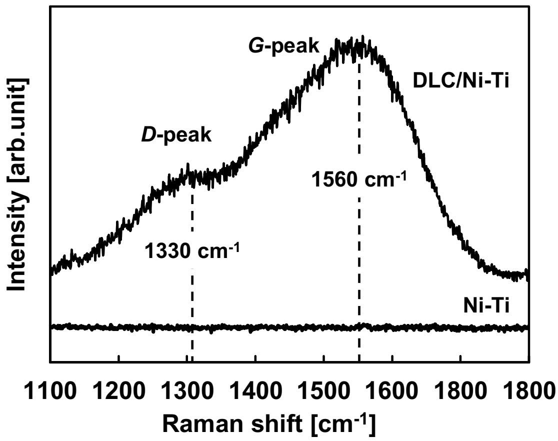

Fig. 5. Raman spectra of DLC/Ni-Ti and Ni-Ti archwires.

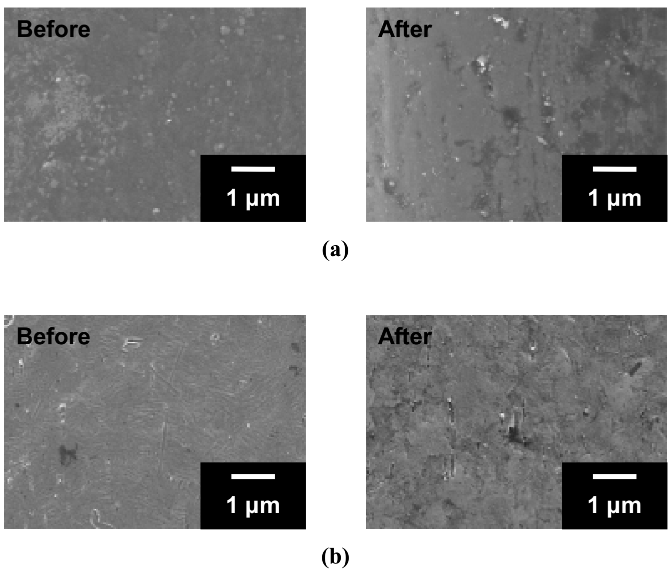

Fig. 6. SEM images of the archwire surface before and after the immersion test in physiological saline at 37°C for six months. (a) DLC/Ni-Ti archwire. (b) Ni-Ti archwire.

before and after the immersion test for six months.

Table 1 shows the concentrations of Ni ions in the physiological saline solution, which were released from the immersed archwires. These concentrations were measured by MIP-MS. In the immersion tests, the amount of Ni ion release was reduced by 80% by using a DLC film coating. DLC films have the ability to act as fluid and vapor transport barriers,[6,17] so the coating inhibited the Ni ion release. Eliades *et al.* reported that Ni ion release from Ni-Ti alloy orthodontic archwires was found to have

Table 1
Concentrations of Ni ions released from the orthodontic archwires.

	Five days at 85°C	Six months at 37°C
DLC/Ni-Ti archwires	50 ppb	150 ppb
Ni-Ti archwires	250 ppb	950 ppb

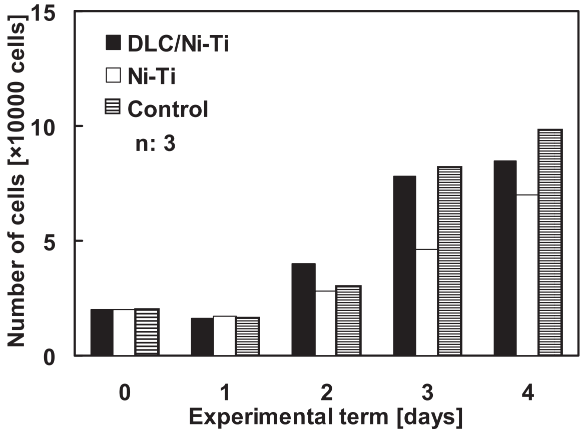

Fig. 7. Relationship between DLC film coating and cell growth over time.

no measurable effect on the viability and physiology of periodontal ligaments and gingival fibroblasts in an *in vitro* study.[18] However, in the same report, they noted that the results reported are questionable because the binding state and formulation of nickel derivatives play a pivotal role in modulating biological reactions induced by nickel-containing materials.[18] Moreover, in *in vivo* studies on the use of Ni-Ti alloy in orthodontic devices, several cases of severe inflammatory reactions resulting in contact dermatitis and oral lesions have been reported.[7,13] In our previous work, it was observed that a DLC coating reduced the effect of Ni ion release on cell growth.[19] Therefore, the application of DLC films to prevent Ni ion release is very appropriate because the Ni ion release in Ni-Ti alloys possibly affects their biocompatibility.

3.3. *Relationship between DLC film coating and cell growth*

The Sa3 cells were cultured in E-MEM solution containing immersed archwires, which were cut to 10 mm, for four days. The relationship between the DLC film coating and cell growth over time is shown in Fig. 7. In the case of cells incubated with the Ni-Ti archwire, it was clear that cell growth decreased compared with the control. On the other hand, there is no significant difference between growth of cells incubated with the DLC/Ni-Ti archwire and the control. The results of the cell culture experiment show that the DLC film coating has no significant cytotoxic effect; the cell growth was not affected by the DLC film coating. As a result of the immersion and the cell culture tests, we have shown that the DLC film coating reduced the rate of Ni ion release and inhibited any effect of the Ni-Ti archwire on the cell growth.

4. Conclusions

A DLC film was successfully deposited on Ni-Ti archwires by arc-discharge ion-plating. The DLC film showed highly stable adhesion to the surface of a Ni-Ti orthodontic archwire in a brushing test and immersion tests. Additionally, it was observed that the DLC film coating inhibited the release of Ni ions and the cytotoxic effect of the Ni-Ti archwire on the cell growth. DLC film coatings are expected to provide multiple improvements to the properties of Ni-Ti archwires, and are applicable to dental materials to improve the stability of orthodontic archwires.

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