Investigation of Anti-Corrosive Performance of a Si-Doped DLC-Coated Magnesium Alloy Stent Deposited by RF-Plasma CVD

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The bioabsorbable magnesium alloy stent exhibits a high dissolution rate; therefore, it faces difficulty in achieving long-term vascular support rigidity. Thus, the control of dissolution rate using a diamond-like carbon (DLC) coating exhibiting excellent biocompatibility is studied. A conventional DLC is usually peeled off from the substrate when the stent expands. The Si-doped DLC (Si–DLC) is considered to be an elastic film candidate for solving this problem. However, the effectiveness of dissolution rate control has not yet been clarified. In this research, we intend to verify the corrosion behavior to confirm the possibility of controlling the dissolution rate of a bioabsorbable magnesium alloy coated with a Si–DLC film using a 13.56 MHz radio-frequency (RF) plasma chemical vapor deposition (CVD) apparatus. Further, the corrosion behavior was examined using electrochemical measurement by cyclic voltammetry. It was observed after repeated oxidation-reduction reaction that Si–DLC can not only drastically diminish the corrosion current value and the pH in the physiological saline solution but also suppress the local corrosion unlike the untreated magnesium alloy and DLC. Thus, the possibility of dissolution velocity control was confirmed.

Keywords: Diamond-like carbon, Chemical vapor deposition, Corrosion behavior, Cyclic voltammetry, Magnesium alloy, Stents, Biomaterials, Bioabsorbable materials

1. Introduction

Stents are used to treat coronary artery disease. A stent is a small metallic medical device in the form of a mesh tube. Currently, the used stent materials comprise insoluble metals, including stainless steel (SUS316L) [1], the cobalt chromium (Co-Cr) alloy [2], and the nitinol (Ni-Ti) alloy [3]. However, they remain semi-permanent in a living body, thereby causing several problems, such as inflammation and restenosis (re-blockage of arteries), in the internal organs. This is a major problem for patients [4]. Therefore, it is desirable to use a bioabsorbable material, which can gradually decompose and get absorbed into the body, as the stent material [5]. Recently, research has been conducted to apply the Mg alloy as a medical bioabsorbable metallic material to develop stents [6-11]. Unfortunately, because Mg is a highly active metal, it exhibits a high rate of corrosion, which makes it difficult to achieve the required rigidity to support blood vessels for several months. Further, new alloys and various surface treatments have been developed to improve the corrosion resistance [12,13]. However, the fundamental problems have not yet been solved.

In this regard, corrosion is expected to be controlled by applying a diamond-like carbon (DLC) coating that exhibits excellent corrosion resistance and that has been clinically proved to be a biomaterial [14]. DLC is an amorphous carbon film comprising hexagonal (sp²) carbon and cubic (sp³) carbon [15] and exhibits outstanding properties such as biocompatibility, corrosion resistance, low friction, and high hardness. Thus far, DLC has been mainly used in industrial fields [16-
In addition, DLC can be deposited into a film for coating a material at a low temperature to reduce the thermal effect on that particular material. Currently, research on the applications of DLC is progressing in various fields, such as dental domains [19,20] and endovascular therapeutical instruments, because of the aforementioned mechanical properties, good blood compatibility, and low-temperature film deposition. The antithrombotic properties and prevention of the restenosis of DLC-coated stents have been confirmed in animal experiments (in vivo) and clinical trials of a human, suggesting their biocompatibility and safety [21-24]. However, stents tend to suffer large plastic deformation during implantation, and conventional DLC exhibit a risk of cracking and peeling off of the film from the substrate.

In a previous study, we have reported that the addition of Si to DLC enables substrate deformation because of the reduction of the Young’s modulus of the film [25]. Furthermore, although a passivation film comprising silicon oxide is present on the Si-doped DLC (Si–DLC), the passivation is caused again by the exposed Si even if this passivation film is broken [26-28]. Thus, Si–DLC can be expected to improve the corrosion resistance when compared with that exhibited by normal DLC. However, research on Si–DLC has mainly been conducted in the fields of tribology and mechanics. Further, there are only a few reports about the corrosion behavior of the Si–DLC-coated Mg alloys, and its effectiveness for application in bioabsorbable stents has not yet been elucidated.

In this study, we examined the possibility of controlling the dissolution rate of a bioabsorbable Mg alloy stent by evaluating the corrosion behavior, including the redox properties of the Si–DLC-coated AZ31Mg alloy, by performing an electrochemical measurement using cyclic voltammetry (hereinafter referred to as the CV method).

2. Materials and method

2.1. Preparation of Mg alloy specimens with DLC coating

The AZ31Mg alloy (AZ31) with a disk-shaped form having dimensions of φ 10 mm × t 1 mm was considered to be the specimen. Its chemical composition is presented in Table 1. Before film formation and before conducting the experiments, ultrasonic cleaning was performed in hexane for 15 min to achieve degreasing. Using this specimen, the DLC-coated AZ31 (hereinafter referred to as DLC/AZ31) and the Si-doped DLC-coated AZ31 (hereinafter referred to as Si–DLC/AZ31) were prepared.

Table 1. Chemical composition of bare AZ31 magnesium alloy specimens (wt%).

| Element | Mg | Zn | Al | Mn |
|---------|----|----|----|----|
| Percent | Bal.| 0.87| 2.97| 0.36|

Figure 1 schematically depicts the apparatus. A parallel plate type 13.56 MHz radio-frequency (RF) plasma chemical vapor deposition (CVD) apparatus was used for achieving DLC film deposition. The conditions of film deposition are presented in Table 2. Before Ar ion bombardment and DLC film deposition, the pressure in the inside of the chamber was evacuated to $7.0 \times 10^{-3}$ Pa. Ar gas was introduced at 10 sccm using a mass flow controller.
and Ar ion bombardment was performed. Subsequently, the Ar gas in the chamber was exhausted, and CH₄ gas was similarly introduced at 10 sccm to achieve DLC film deposition. The pressure was maintained to be 5 Pa for both Ar ion bombardment and film deposition, and the RF power were 20 and 70 W for Ar ion bombardment and film deposition, respectively.

Further, the Ar ion bombardment time and the film deposition time were 60 and 10 min, respectively. The conditions for the formation of the Si–DLC film were the same as those for the deposition of the DLC film, except that tetramethylsilane (TMS) was used as the gas source instead of CH₄.

2.2. Electrochemical measurement method

Figure 2 presents the schematic of the electrochemical measurement cell. The working electrode, counter electrode, and reference electrode were connected to a potentiostat device (HAB-151A made by Hokuto Denko) that can measure the current while controlling the potential. The three electrodes were immersed in an aqueous solution, and the current was measured by increasing/decreasing the potential at constant speeds. The working (specimen) electrode was a SUS304 steel wire soldered to the back side of the specimen as well as covered with the silicone tube and the room-temperature vulcanizing silicon rubber. A platinum mesh electrode was used as the counter electrode, and an Ag/AgCl (internal solution: 3 M NaCl) electrode was considered to be the reference electrode. Further, 500 ml of 0.9% mass NaCl solution that was prepared using ultrapure water and sodium chloride was used as the test solution at 310 K. The test solution was maintained at this temperature using a hot stirrer, and the dissolved oxygen was saturated by blowing air and stirring. Further, a sweep rate of 5 mV s⁻¹ was adopted as the measuring condition, and the polarization range was observed to sweep from −1.55 V, i.e., the natural potential ($E_{corr}$) of each sample, to −1.1 V from the anode side. Thereafter, the cathode side was swept up to −2.0 V and was finally swept up to the starting point of −1.55 V. The potential and current were measured using a digital multimeter (VOAC7523H manufactured by Iwasaki Tsushink). The pH change in the 0.9% NaCl solution during sweeping was measured using a pH meter (392R, manufactured by As One). Subsequently, the surface of the sample after corrosion was observed using a scanning electron microscope (SU8010, manufactured by Hitachi Seisakusho). Dynamic viscoelasticity measurement (NanoDMA method: Nano Dynamic Mechanical Analysis) was performed by the nanoindentation method to measure the elastic modulus of films. A nanoindentation device (Triboindenter Ti-950 manufactured by Hysitron) was used for performing the measurement.

3. Results and discussion

3.1. Corrosion behavior using a cyclic voltammogram

The changes in corrosion behavior owing to redox reactions were verified by repeating the potential scanning five times. Figure 3 depicts the cyclic voltammograms of bare AZ31, DLC/AZ31, and Si–DLC/AZ31 up to five cycles. The horizontal axis denotes the potential during polarization, and the vertical axis denotes the current value. In the cyclic voltammogram, + denotes positive polarization, whereas − denotes negative polarization.

In case of bare AZ31, different current waves were obtained by sweeping in the 1st cycle in the positive and negative directions with the same potential in the anode region of −1.1 to −1.55 V. This phenomenon is presumed to be caused by the active state region. The active state region is the area at which the reaction proceeds extensively and the reaction rates are observed to differ. The anode peak currents were 43.5, 1.3, and 0.6 mA during the 1st, 3rd, and 5th cycles, respectively. Additionally, the current value decreased significantly after three cycles. It is considered that the decrease in the current value can be attributed to the deposition of magnesium hydroxide on the sample surface as corrosion progresses [29], causing passivation.

In case of DLC/AZ31, the anode peak current after three cycles also decreased similar to that in...
bare AZ31 but to a lesser extent. This could be probably attributed to the fact that the passivation was inhibited by the remaining DLC even though DLC underwent peeling off. However, current waves owing to the active state region observed in the 1st cycle of bare AZ31 were confirmed after three cycles. It can be inferred that this current wave was generated when the surface of the AZ31 Mg alloy was newly exposed as the film peeled off and the reaction rapidly proceeded again.

The anode peak current did not exhibit a drastic decrease in case of Si–DLC/AZ31, indicating that the passivation was inhibited by the film residue. Furthermore, the active state region observed in DLC/AZ31 after three cycles was considerably small.

Table 3 presents the peak current of each sample in the 1st, 3rd, and 5th cycles. During the 1st cycle, DLC/AZ31 exhibited a 52% decrease in anode peak current from 43.5 to 20.9 mA and a 54% decrease in cathode peak current from −28.9 to −13.3 mA when compared with those exhibited by bare AZ31. This result suggested that the application of DLC coating suppressed the dissolution and the reduction reaction. Furthermore, the cathode peak current after five cycles was decreased by 39% from −22.7 to −13.8 mA when compared with that in bare AZ31. Additionally, it is suggested that DLC/AZ31 continued to inhibit the reduction reaction even though the peeling off advanced. However, Si–DLC/AZ31 denoted a decrease of 73% in the anode peak current from 43.5 to 11.9 mA and a decrease of 79% in the cathode peak current from −28.9 to −6.0 mA in the 1st cycle when compared with those in bare AZ31. The current value of Si–DLC/AZ31 is considerably smaller even while comparing this value with that of DLC/AZ31. This result indicates that the reduction and dissolution reactions were suppressed and that the corrosion resistance was improved when compared with that of DLC/AZ31.

### 3.2. pH change and corrosion dependence

Because the pH in the aqueous solution is dependent on the dissolution of hydrogen and Mg ion by cathode and anode reactions, respectively, the pH was measured while scanning the potential in the 1st cycle. Figure 4 depicts the pH change in the physiological saline solution in the 1st cycle. When the anode region from −1.55 to −1.3 V was examined, DLC/AZ31 and Si–DLC exhibited almost similar pH values to that of bare AZ31. However, the pH of bare AZ31 increased rapidly from −1.3 to −1.55 V even though the increase in that of DLC/AZ31 was moderate. After sweeping

### Table 3. List of the peak anodic and cathodic currents in 1st, 3rd, and 5th cycles of bare AZ31, DLC/AZ31, Si-DLC/AZ31 specimens.

| Specimens     | 1st cycle | 3rd cycle | 5th cycle |
|---------------|-----------|-----------|-----------|
|               | Anode (mA) | Cathode (mA) | Anode (mA) | Cathode (mA) | Anode (mA) | Cathode (mA) |
| Bare AZ31     | 43.5      | -28.9     | 1.3       | -24.7       | 0.6        | -22.7        |
| DLC/AZ31      | 20.9      | -13.3     | 15.5      | -13.6       | 9.3        | -13.8        |
| Si-DLC/AZ31   | 11.9      | -6.0      | 2.9       | -5.9        | 0.9        | -6.8         |
up to the 1st cycle, the pH of saline was 8.97, 7.23, and 6.81 for bare AZ31, DLC/AZ31, and Si–DLC, respectively. Further, the pH decreased by 2.16 when compared with that of bare AZ31 by applying the Si–DLC coating. The increase in pH under anodic polarization in any of the samples can be considered to be caused by the reduction of water associated with the oxidation of Mg$^+$ to Mg$^{2+}$ [13] and the generation of OH$^-$. Generally, the corrosion reaction of magnesium in a neutral environment can be expressed using the following equation [30]:

$$\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \quad (1)$$

This reaction can be further described in detail as follows:

$$\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \quad \text{(Anodic reaction)} \quad (2)$$

$$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad \text{(Cathodic reaction)} \quad (3)$$

$$\text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 \quad (4)$$

As corrosion progresses, the generation of hydrogen gas and pH increases because of the presence of the OH$^-$ ions; further, Mg(OH)$_2$ membrane is produced from the Mg$^{2+}$ and OH$^-$ ions. Therefore, during the pH measurement, the reduction and dissolution reactions were clearly suppressed in Si–DLC/AZ31 when compared with those in DLC/AZ31, suggesting an improvement in corrosion resistance. Furthermore, the corrosion tendency results are in agreement with the cyclic voltammogram results.

### 3.3. Corrosion surface morphology

Figure 5 depicts the appearance of each sample after corrosion. Bare AZ31 presented an uneven corrosion with a circular mottled pattern. This localized corrosion (pitting corrosion) of bare AZ31 can be generally considered to be galvanic corrosion [31-33]. During galvanic corrosion, the corrosion of metals with low potentials is promoted by the difference between the corrosion potentials of different types of metals. AZ31 is a two-phase alloy, where the β phase of Mg17Al12 is dispersed in the α phase, which is a matrix phase mainly comprising Mg [34]. It is considered that non-uniform corrosion mainly progresses because of the preferential corrosion of the α phase.

In contrast, it was confirmed that the corrosion of DLC/AZ31 generally progressed because of the formation of pinholes on the film [35] and that the corrosion gradually progressed based on the pinholes present on the surface, resulting in uniform corrosion on the entire surface. In addition, it is estimated that the galvanic corrosion was suppressed by reducing the exposure of the metal surface using DLC coating. However, peeling off of the film was observed on the entire metal surface.

Although corrosion was observed only in a part around the pinholes in Si–DLC/AZ31, the surface is different from the DLC/AZ31 surface. Further, several parts that did not exhibit peeling off of the film could be observed after corrosion. The exposed
area of the metal surface was observed to be the smallest.

Based on the aforementioned results, Fig. 6 depicts the process of film separation (peeling off). First, during film deposition, a compressive residual stress is generated inside the film. Thereafter, corrosion proceeds from the pinholes present in the film, and the AZ31 Mg alloy is dissolved as the scaffold of the film. Meanwhile, the film loses its scaffold, and cracks are generated by the compressive residual stress in the film, inducing separation. However, because Si is added to DLC in Si–DLC, its elastic modulus is lower than that of DLC. An elastic film is formed, thereby preventing separation. The elastic moduli of DLC and Si–DLC were 105.7 and 100.8 GPa, respectively, suggesting the consideration of the separation process.

4. Conclusion
In this study, the AZ31 Mg alloy was coated with DLC and Si–DLC using a RF plasma CVD method. The change in the corrosion behavior was verified by the CV method. The following main results were obtained. The results of cyclic voltammograms that were recorded up to five cycles indicated that Si–DLC inhibited passivation and contained a small active region. Si–DLC was effective for controlling the corrosion rate. The results of pH measurement and the 1st cycle in cyclic voltammogram suggested that Si–DLC considerably inhibited the dissolution and reduction reactions when compared to DLC; thus, the corrosion resistance was improved. According to the results of the samples after being subjected to corrosion at the 1st cycle, the separation of the film exhibiting uniform corrosion progressed in case of DLC; however, the separation of the film in the Si–DLC film stalled after corrosion. Because Si–DLC exhibited a lower modulus of elasticity than that exhibited by DLC, it can be inferred that its ability to follow compressive residual stress in the film was enhanced.

According to the aforementioned results, vascular support rigidity can be achieved by enabling dissolution rate control and by preventing film separation during the expansion of the stent when the Si–DLC coating is applied to a stent.

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