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Electrochemical corrosion behavior of a non-vascular, bi-stent combination, surgical esophageal nitinol stent in phosphate-buffered saline solution

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ABSTRACT

In the present work, the corrosion behavior of a bi-stent combination, which is the combination of an uncoated outer stent and silicone-coated body stent, was assessed by the use of electrochemical methods in phosphate-buffered saline at 37 °C. Although each stent comprising the bi-stent combination showed favorable corrosion properties, the bi-stent combination showed significant decreases in these corrosion properties. Corrosion was concentrated on the uncoated outer stent of the bi-stent combination. The cathodic reaction was activated on the outer stent of the bi-stent combination by the galvanic effect, and the hydrogen generated was detrimental to the surface film on the outer stent. In addition, hydrogen had a synergic effect with chloride and accelerated the corrosion reaction on the outer stent.

1. Introduction

Stents are small expandable tubes used to treat narrowed or weakened vascular and non-vascular parts of the body. Depending on the type of vessel, they are classified as vascular or non-vascular stents [1]. Non-vascular stents are a family of devices used for a variety of applications including biliary, esophageal, colonic, bronchial, and tracheal implantations. The use of non-vascular stents in these applications is fueled by a number of market drivers. Specifically, non-vascular stents have increasing applications in esophageal diseases, owing to an ageing population, changing lifestyle habits, and environmental conditions [2,3]. With the increase in the usage of esophageal stent, various types, shapes, and materials have been developed.

One of the widely used stent materials is nitinol (NiTi), which contains nearly equi-atomic proportions of nickel and titanium [4,5]. This alloy was advanced in the 1970s and was very soon applied to biomedical purposes, first in orthodontic treatments, and later in cardiovascular surgery as stents due to its unique properties of shape memory and superelasticity [6–8]. As a biomedical material, nitinol has to demonstrate high corrosion resistance for suitable mechanical properties [9,10] in various solutions used for biological research such as phosphate-buffered saline (PBS) and Hanks' physiological solutions. However, nitinol is inferior to titanium, Co-Cr-Mo alloy, and even stainless steel with regard to corrosion resistance [7]. Also, since it contains ~50 at.% of nickel, which is a known allergen, the problem of nickel release is significant [7]. Thus, the corrosion resistance of nitinol stent is an important consideration for application to the human body.

In particular, nitinol has susceptibility to localized corrosion [11], namely crevice and pitting corrosion, which can be a drawback for its use in vivo and should be avoided. In previous studies, the breakdown potential of nitinol was indicated with values between 240 and 1000 mV vs. a saturated calomel electrode (SCE) [12–15], which might be related to the dependence of localized corrosion resistance on surface conditions, stent design [16], and rod diameter [12]. A huge tendency for crevice corrosion was shown for specimen with small diameters, since the contacts between the nitinol rods and mounting resin were more prone to defects [12]. Therefore, various parameters should be considered in designing and manufacturing nitinol stents.

As mentioned above, with the recent increase in the usage of esophageal stents, there are many issues associated with their use, such as migration of the stent, positioning difficulties, stent fracturing, and restenosis [16]. Generally, the silicone membrane is coated on the inner surface of an esophageal stent by a dip-coating or electrospinning method to facilitate insertion and deployment through production of a surface smoother [17,18]. A stent with a rough surface would be more difficult to insert and deploy due to the friction between the stent wire and the inner wall of the esophagus. However, if the surface of the stent is too smooth, it increases the tendency for stent migration due to the lower attachment surface area for the surrounding tissues [19]. To solve this problem, the bi-stent combination was designed. As shown in Fig. 1, the bi-stent combination is composed of a silicone-coated body (inner) stent part and an outer stent, unlike the general single-layer

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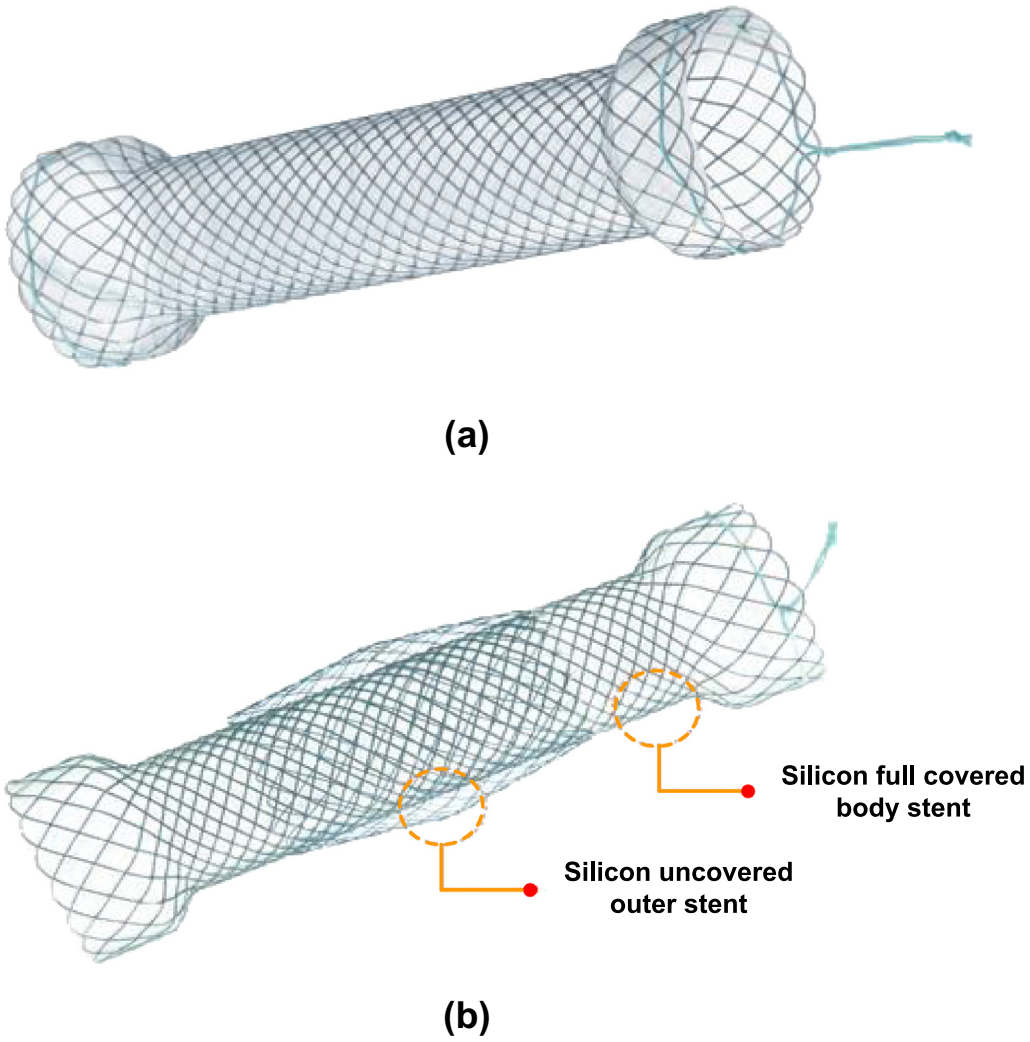

Fig. 1. Images of (a) general silicone coated single and (b) bi-stent combination esophageal stent.

stent. The uncoated outer stent wire allows it to interact easily with the tissue of the inner wall of the esophagus, helping prevent stent migration [20–22].

However, the design and change in surface properties of a stent are important factors for corrosion resistance, especially localized corrosion; therefore, the evaluation of corrosion behavior and elucidation of the corrosion mechanism should be prerequisites for application of this stent type. Thus, in this study, the corrosion behavior of a bi-stent combination was evaluated, and the corrosion mechanism in PBS solution was investigated by electrochemical tests.

2. Materials and methods

2.1. Test materials and processing

Commercially available binary nitinol wire was supplied by Special Metals Corporation of New Hartford, NY, USA and Shape Memory Applications of San Jose, CA, USA. Two wires were supplied in the mechanically polished condition, with diameters of 0.229 and 0.178 mm. The diameter of the outer stent was designed to be 0.178 mm, because a thicker diameter increases the volume of the stent and the contact area with the inner wall of the esophagus, which can increase the difficulty of insertion and deployment in surgery. Each wire was woven according to the designed stent size and shape (outer and body stents), and the total wire lengths used for the outer and body stent were approximately 6000 and 9600 mm, respectively. Therefore, the areas of the stents were 0.148 and 0.394 cm^2, respectively. For the representative shape setting, the heat treatment was conducted at 500 °C using a salt bath for 5 min. The heat treatment was followed by oxide removal in 20% nitric acid solution at 80 °C for 13 min, ultrasonic cleaning in deionized water for 20 min, passivation treatment in ammonium nitrate (NH_4NO_3) solution at 80 °C for 20 min, and ultrasonic cleaning in deionized water for 20 min on the outer and body stents. Before combining the outer and body stent, the body stent was subjected to liquid silicone coating by the dip-coating method, and then it was cured for 30, 45, and 135 min at room temperature, 80 °C, and 150 °C, respectively, to evaporate the solvent. Liquid silicone coating solution (18 wt%) was consisted of silicone mixture (Nusil Silicone Technology) with acetone and xylene (1:1) solvent, and it was dissolved by magnetic stirring. Also, the commercial primer (Nusil Silicone Technology) was coated at 50 °C for 30 min according to the instruction before silicone rubber coating. Lastly, the outer stent was connected to the middle section of the body stent by a stitching fiber to create the bi-stent combination (diameter: 20 mm, length: 15 cm). Morphology of silicone coating on the stent was analyzed by scanning electron microscopy (SEM).

2.2. Electrochemical measurements

Electrochemical measurements were performed in a conventional