Corrosion Behavior of Stents Coated with Gold and a-SiC:H

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Summary

The optimization of the functional characteristics of stents includes the evaluation of surface coatings of different types and for different purposes. For example, the X-ray visibility of the stent can be increased by coating a core body consisting of medical-grade stainless steel (316L) with a thin gold film. Since the stent consists of two different metals and is conceived for use in an electrolyte (blood), corrosion behavior should be investigated. This paper investigates the influence of gold and silicon carbide coatings on the corrosion behavior of stents with 316L as a core body material. The stents studied were coated with a-SiC:H, gold (as an X-ray marker coating at the stent ends), or a combination of the two. In case of the latter, the gold-covered stent was coated completely with an a-SiC:H layer. Thanks to the additional a-SiC:H coating, the results show that the gold coating has no negative influence on the corrosion behavior of the entire system.

Key Words

Corrosion, stent, gold, a-SiC:H

Introduction

In recent years, stent implantation has become an established therapeutic procedure for the minimally invasive treatment of stenotic coronary arteries. Along with the optimization of the geometric design, hybrid designs have been pursued to further improve the functionality of the implant by means of different surface coatings. Along with coatings improving the hemo- and biocompatibility, coatings that increase the X-ray visibility are of particular importance.

More than 90 % of the coronary stents currently available on the market consist of medical-grade stainless steel (316L). Since this alloy consists primarily of metals with low atomic numbers, and the X-ray density is scaled at approximately the third power of the atomic number, coating the stent with a material of a higher atomic number will increase the X-ray visibility. Due to its relatively high atomic number, its favorable ductility, and the possibility of thin-film deposition using inexpensive galvanic procedures, gold is used as a coating material.

When using the combination of 316L and gold in liquid, electrolytic media such as blood, the corrosion resistance of the system comes into question. The main reasons for this are contact and crevice corrosion. The corrosive attack in particular could lead to the destruction of the implant or to a release of metallic ions.

Along with the potential problem of corrosion, there is the question of bio- and hemocompatibility of gold that is in direct contact with the biological environment. While some authors do not see any deleterious interactions between gold and the vessel wall [1,2], a significant thrombogenic effect has been attributed to this material in other publications [3,4]. This article examines in particular the corrosion behavior of gold-covered stents that have been coated with an additional, amorphous silicone carbide film that is known to be antithrombogenic (a-SiC:H) [5], and which prevents direct contact between the gold coating and the biological environment.

Materials and Methods

The core body of all stents studied (all Tenax coronary stent, Biotronik, Germany) consisted of medical-grade

stainless steel (316L). The measurements were performed for different variants of this stent:

- Group a: 316L stents without coating.
- Group b: 316L stents with an a-SiC:H coating covering the entire stent [6].
- Group c: 316L stents with X-ray markers on the ends. The X-ray markers consisted of approximately 7µm-thick gold films galvanically applied to both ends at a length of about 2 mm.
- Group d: Stents like c), but with an additional a-SiC:H coating completely covering the gold-marked stent.

All stents were expanded to the maximum possible diameter of 4.5 mm with a balloon catheter used in clinical practice.

The recommendations in DIN EN 12006-3 were consulted as a guide for the corrosion tests [7,8]. The principal configuration portrayed in Figure 1 was used as a measurement cell. The stents were contacted at one end. In order to avoid any influence of the contacting point on the measurement, only one half of the stent was immersed in the electrolyte. The tests were performed in an isotonic saline solution at 37 °C in the ventilated measurement cell. Carbon was used as a counter-electrode, and a calomel electrode was used as reference. The potential-values given in the following are compared to the reference potential of the standard hydrogen electrode. The current density was determined from the current values measured at the submerged surface of the stent (approx. 0.6 cm^2).

The free corrosion potential (i.e., open circuit potential, OCP) is determined by submerging the samples in the electrolytes for 24 hours and measuring the potential over this time, the samples not being exposed to electric shocks during this period.

The breakdown potential U_D and the repassivation potential U_{Rep} are then determined via cyclical voltammograms. Starting point being the open circuit potential, the stents were exposed to a positive potential increasing at a rate of 30 mV/min. The breakdown of passivity can be determined as an large increase in current. Directly after the breakdown potential had been reached, the potential was again reduced at a rate of 30 mV/min in order to study the repassivation behavior. The currents were re-measured. Thus, repassivation was proven to consist of a current-drop to values

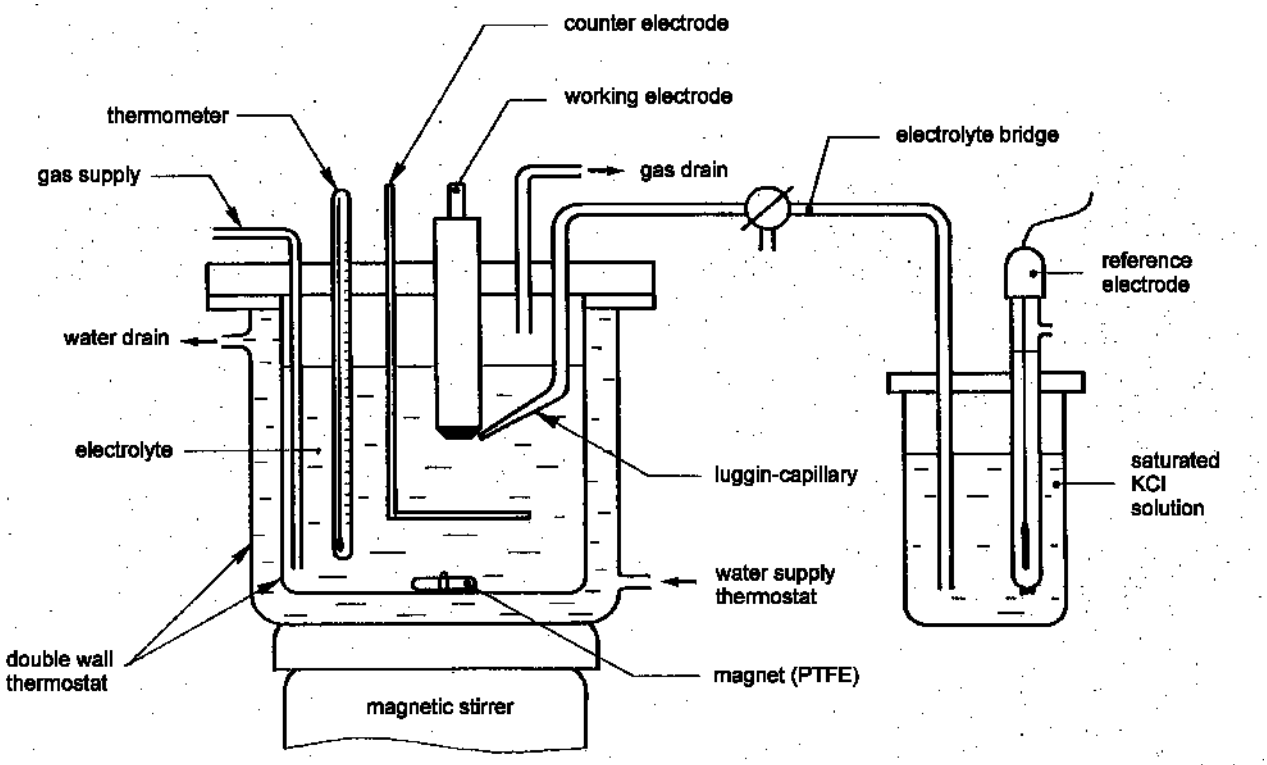

Figure 1. Principal configuration of the measurement cell.

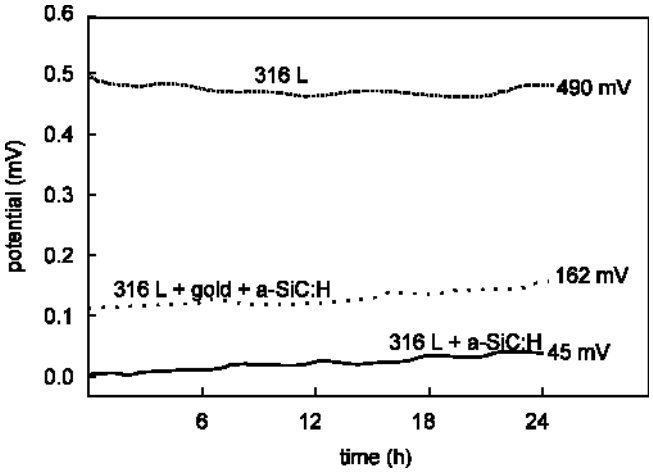

Figure 2. Open circuit potential measurements on stents with different coatings.

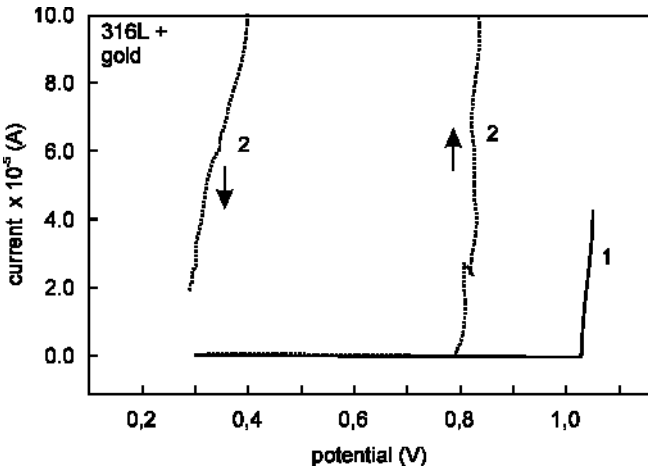

Figure 3. Voltammograms for stents with gold markers (group c).

comparable to those before breakdown.

In order to analyze how fast a stationary protective layer is formed, the samples were immersed into the electrolyte and different electrode potentials in the range of the breakdown potential were applied over a period of 24 h, while measuring the course of the current over time. The saline solution was tested via Inductive Coupled Plasma (ICP) for the presence of metallic ions (Fe, Cr, Ni, Si).

Results

Figure 2 shows the results of the open circuit potential measurements for representative samples of the groups a (316L), b (316L + a-SiC:H) and d (316L + Gold + a-SiC:H). A comparison of the measured values for the sample groups a (approx. 490 mV) and b (approx. 45 mV) shows a clear drop of the OCP due to the a-SiC:H coating. Even with a gold coating between the core body and the a-SiC:H layer (sample group d; OCP approx. 162 mV), a markedly lower open circuit potential results as compared to the uncoated stent from group a. In all 3 cases, the potentials hardly changed over 24 hours.

The somewhat higher value of the open circuit potential of sample group d (316L + Gold + a-SiC:H) in comparison to group b (316L + a-SiC:H) is due to micro-cracks in the thin a-SiC:H coating (approx. 80 nm), which can occur in bridging areas by extreme stretching (approx. 30 %) during dilatation to the maximum allowable diameter of 4.5 mm. In these places, the potential value can lead to slightly higher values due to the gold underneath. However, the electron microscope was not able to detect any detachments of the a-SiC:H coating.

Figures 3 to 5 show voltammograms for stents in groups b, c and d, with two measurements each, one of which documents in addition the repassivation behavior of the samples. The breakdown potentials U_D and repassivation potentials U_{Rep} determined from these current-potential plots are summarized in Table 1.

The difference of the breakdown potentials U_D within the sample groups is caused by small differences in the end conditions of the individual samples after expansion. Nevertheless, the breakdown potentials lie above 500 mV for all samples studied. In addition, all samples were able to repassivate, when the external potential decreased to values between 300 mV and 500 mV. Therefore, initiated corrosion does not lead to destruction of the stent or coating peel off, but is stopped once the potential drops below the repassivation potential.

In the potential range near 500 mV, which is typical for the beginning of the breakdown, the corrosion behavior is studied more closely in the form of immersion tests at constant potentials. The results for sample group d (316L + Gold + a-SiC:H) are summarized in Figure 6 and Table 2.

Measurements were performed at potentials of 450 mV and 500 mV. Despite the sharp increase of the current at the beginning, the stationary current, which sets in after 1 to 2 hours, is decisive for the long-term behavior.

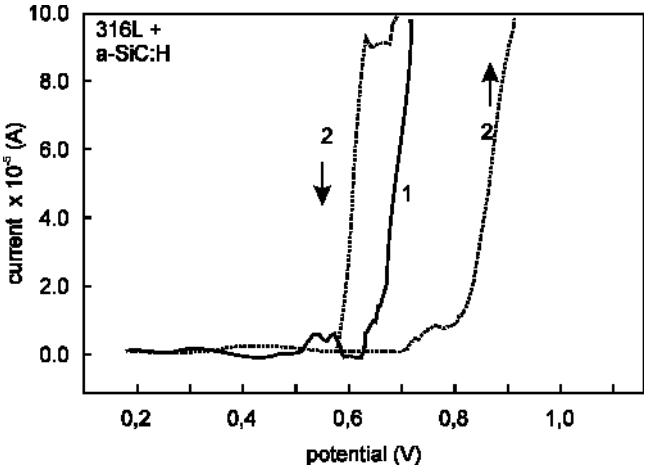

Figure 4. Voltammograms for stents with a-SiC:H (group b).

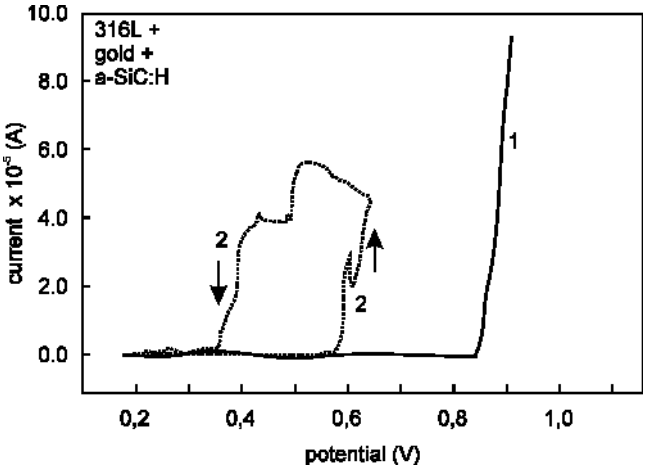

Figure 5. Voltammograms for stents with gold markers and a-SiC:H (group d).

At 450 mV, a current value of 45 µA is reached temporarily, but drops back to values between 0.5 µA and 28 µA after 1 - 2 hours. Thus, it can be observed that, after applying a potential of 450 mV, the formation of a passive layer is not disturbed by a corrosive attack.
At 500 mV, a qualitatively similar behavior can be observed. However, the initial corrosion current, with a peak value of about 320 µA, is markedly higher than at 450 mV. The current variations in the stationary phase are correspondingly higher at 500 mV after 1 - 2 hours, with values up to 220 µA. After the ICP analysis, which is summarized in Table 2, a correspondingly higher iron content was found in the electrolytes after the immersion tests due to the significantly higher corrosion current at 500 mV than at 450 mV in the stationary status.

Discussion and Conclusion

The main purpose of this study was to investigate the corrosion behavior of stents consisting of medical-grade stainless steel (316L) with a thin (approx. 7 µm) gold layer over a length of approx. 2 mm, and an additional a-SiC:H coating covering the entire surface. For comparison, uncoated samples or samples coated with gold or a-SiC:H were included.
The open circuit potential of samples coated with a-SiC:H was significantly lower than the value for uncoated samples (490 mV). Without a gold coating underneath, a value of 45 mV was attained; with a gold coating, a higher value of about 162 mV was measured. Thus, the a-SiC:H coating provides a significant drop in the open circuit potential. This potential is of paramount importance for corrosion resistance, since it depends directly on the difference between the open circuit potential and the breakdown potential.

Sample	State	U_D (V)	U_{Rep} (V)
1	316L + gold	1,03	-
2	316L + gold	0,78	0,30
1	316L + a-SiC:H	0,58	-
2	316L + a-SiC:H	0,70	0,58
1	316L + gold + a-SiC:H	0,84	-
2	316L + gold + a-SiC:H	0,58	0,37

Table 1. Breakdown potentials U_D and repassivation potentials U_{Rep}.

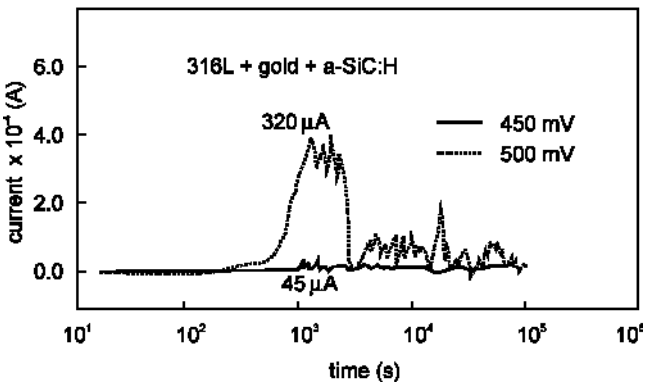

Figure 6. Current-time curves at constant potentials.

	Potential	450 mV	500 mV	Detection limit (ppm)
ICP analysis	Cr (ppm)	0.043	0.196	0.0012
	Fe (ppm)	0.216	0.825	0.0023
	Ni (ppm)	0.077	0.431	0.0138
	Si (ppm)	< detection	0.038	0.0032
Immersion test	Peak current (μA)	45	320	
	Passivation time (h)	1,1	2	
	current (μA) Fluctuation	0.5 - 28	0.5 - 220	

Table 2. Evaluation of current-time curves and ICP-analyses at constant potentials.

Furthermore, breakdown and repassivation behavior were provided by recording cyclical voltammograms. The beginning of corrosion was shown to occur at an external potential of about 500 mV. The measurements also showed that all studied coating systems repassivated after the external potential was reduced below the breakdown potential, which means that corrosion stops as long as external conditions no longer cause it to occur.

Finally, the interesting potential range for the initiation of corrosion (approx. 500 mV) was further examined by immersion tests at a constant potential. Despite the higher peak values and the higher values for the current in the stationary state, even after the immersion test at 500 mV, the ICP measurements in the electrolyte showed concentrations of the elements Fe, Cr, Ni, and Si that were more than an order of magnitude below the limit values of 10 ppm named in the guideline ISO 109993-15 [9].

In summary, it can be stated that an increase in corrosion resistance has been achieved, especially due to an a-SiC:H-conditioned drop in the open circuit potential. An additional gold coating does not have a significant influence on the corrosion behavior.

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