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Microstructuring of stainless steel implants by electrochemical etching

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Abstract The effects of electrochemically enhanced etching on stainless steel coronary stent surfaces have been investigated in respect to their applicability as surface modifications prior drug-coating. Two methods have been investigated, one basing on grain boundary etching with diluted HNO_3 and the other one on hydrochloric acid etching. The etching current was in the range of 30–200 mA which accounts for 0.34–2.28 mA/mm^2 surface. Grain boundary etching produced a micro-furrowed surface providing volume for the coating drug. The theoretical volume offered by the furrows was calculated on the basis of laser perthometry and was determined to be 0.146 mm^3/cm^2. With the hydrochloric acid etching method it was possible to generate an evenly rough, terraced surface. Both surfaces have been coated with Rapamycin in ethanol (20 mg/mL) and examined under SEM after dilatation. It was shown that a uniform drug layer is maintained after dilatation of the stent and little flaking is visible. Quantification of the amount of Rapamycin yielded 21.4 μg/mm^2 for the electropolished stents, 36.6 μg/mm^2 for the grain-boundary etched stents and 27.7 μg/mm^2 for the hydrochloric acid etching after dilatation. For the grain boundary etched stents an improved drug adhesion was found, while the hydrochloric acid etchings resulted in a deterioration of the adhesion properties.

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Introduction

Overview

In recent years the long term results of percutaneous transluminal angioplasty as a treatment of atherosclerotic stenoses have markedly improved by the use of drug coated metallic stents [1, 2]. Due to the requirement of a decelerated release kinetic and problems with the adhesion of the coatings, however, the use of an additional polymer coating is normally inevitable [3]. Polymer coatings are difficult to apply and carry the risk of releasing detached particles into the blood due to insufficient adhesion to the stent surface [3, 4]. Therefore, the ideal stent surface would be a microstructured surface that has good adhesion properties, provides depot volume and provides a decelerated release kinetic. A common method of surface modification in order to increase adhesion is grit blasting. Grit blasted surfaces, however, do not provide depot volume for a drug and the procedure imposes mechanical stresses, which is problematic when applying this procedure to damageable parts like stents. An interesting alternative is given by chemical etching techniques. Some research has been performed on the applicability of chemical etching in order to improve the surface properties of coronary stents. However due to the low roughness achievable with mere chemical etching techniques none of these

techniques were put into practice. In this work the effects of electrochemical etching techniques on stainless steel stent surfaces have been investigated. In contrast to conventional microstructuring etch techniques where structures are imposed on the substrate surface by the use of chemically inert masks [5], this work uses intrinsic material structures to create randomly distributed surface microstructures in a simple process. The principles of this approach are partly adopted from well-known metallographic techniques where electrolytic etching is used in order to show grain structures [6, 7].

The effects of two etching methods have been examined on 316L stainless steel stents: electrochemical grain boundary etching with HNO_3 and electrochemical etching with HCl. The etched stents were analysed with SEM. In case of the grain boundary etched stents generated roughness and removal rate were determined at different etching parameters. In order to evaluate the coating properties, the etched stents were coated with Rapamycin and the amount of drug on the stent after dilatation, as well as the adhesion properties, have been measured. Electropolished stents were used as reference.

Theoretical background

Although electrochemically enhanced etching methods have been used in the field of metallography for decades, very few literature is available in which the theory of these etching processes is described in detail.

A general model describing the molecular processes near the electrode during electrolytic etching has been established by Gouy, Chapman and was advanced by Stern [8]. However these new models do not refer to the different etching rates of intrinsic structures (like grain boundary- and matrix-etching rate). The only references on this topic can be found in a publication by F. Bell and D. Sonon from 1976 [9] concerning grain boundary etching and in ''Metallography, Principles and Practice'' by G. Vander Voort from 1984 [7] see p. 194 referring to pitting corrosion which gives useful information for the understanding of the hydrochloric acid etching method.

Bell and Sonon estimated the selectivity (the ratio of grain boundary- and matrix etching rate) of stainless steel grain boundary etching using a current/voltage diagram. In this diagram the curves of matrix and grain boundaries are very similar while the grain boundary curve shows only a slight offset in 45° direction towards higher currents and towards lower voltages. This results in a very small range of high selectivity. This area is referred to as the ''grain boundary etching range'' in the diagram (Fig. 1).

In [7] the principles of pitting corrosion are analysed on the example of a Fe–Si alloys. In this work triangular- and rectangular-shaped pits were generated as an undesired result of improper electrolytic etching. These pits have been attributed to a non-uniform etching of crystal planes of different orientation.

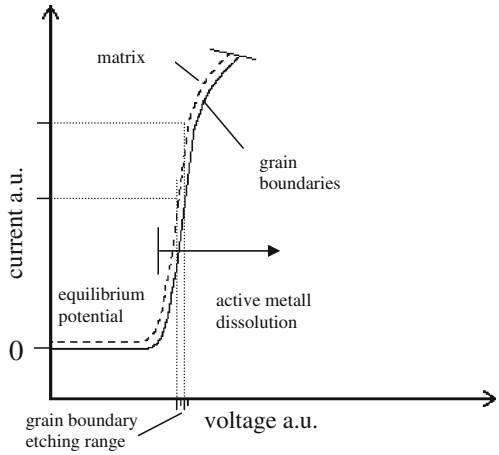

Fig. 1 U/I-diagram of annealed 316L (grain boundaries and matrix) according to [1]

Materials and methods

Materials

Electropolished stents (Translumina GmbH) of the alloy 316L were used having 12 mm length, 120 μm strut thickness and 140 μm strut width. The tube material used for the perthometry roughness measurements was 316L stent raw material (Minitubes, France) with 1.4 mm inner diameter and 120 μm wall thickness. The mean linear intercept grain size of the raw material was determined as 15.8 μm. As basis for the etching solutions served HCl 35% p.a. and HNO_3 65% p.a. (Merck GmbH), respectively. The acids were diluted with demineralised water as follows: 30 mL HCl and 10 mL H_2O for the hydrochloric acid etchings, 40 mL HNO_3 and 25 mL H_2O for the grain boundary etchings.

Etching procedure

The stents were crimped manually on a stainless steel rod of 1.4 mm diameter and placed in the etching solution after 5 min of cleaning with ultrasonic in acetone. The etching time was 10 min for all specimens. Etching was carried out at room temperature. Current was applied by a DC-transformer (Conrad PPS 3003), with the stent used as the anode. A stainless steel sheet served as the cathode. Cathode and anode were separated using two beakers with etching solution connected by a cellulose membrane. Current was measured by an amperemeter at 50–1000 mA current (according to 1.2–3.6 V) with an accuracy of 5 mA. In the case of the hydrochloric acid etching the

solution was stirred during the etching process with a laboratory stirrer at 300 rpm.

Surface characterization

The etched samples were analysed by SEM (Hitachi 4500 N) and mechanical perthometry (Mahr Perthometer M2). The most important roughness value for the grain boundary etchings is the Rz value. This value is most sensitive for discrete indentations as it gives an average of the highest peaks and the lowest valleys. For the hydrochloric acid etchings the Ra values are given, characterizing the average roughness. In case of the grain boundary etching additionally laser perthometry was used for surface characterization. The laser perthometry data have been analysed computer aided (software ODSCAD) calculating the free volume below the zero-area which is given by the average depth of the analysed surface area. Selective stents were embedded in polymer resin in order to produce polished sections of the cross-areas of the stent struts. In case of the grain boundary etched stents the sections were used in order to measure the crevice length and the thickness loss.

Coating and layer analysis

Two stents of each surface modification (grain boundary etched, hydrochloric acid etched and electropolished as reference) were drug-coated in order to compare the coating behaviour. Coatings were performed by a coating system (Translumina, T-SCM 2003) with Rapamycin (99.8%) solved in ethanol (p.a., 99.8%) at a concentration of 20 mg/mL. During the coating procedure the ethanol evaporates so that a layer of pure Rapamycin remains. After coating the stents were delatated at 14 atms. Of each etching procedure three stents were used for Rapamycin quantification and three stents were used for adhesion tests. For the adhesion tests an implantation was simulated by implanting the stent into a silicone tube of an artificial blood circuit. After implantation the section with the stent was cut out and the tube was sliced in order to remove the stent. For quantification the Rapamycin was washed off in two steps with 2 mL ethanol each and the total amount of Rapamycin was determined by UV–Vis spectroscopy. For SEM analysis the stents were sputter deposited with gold to prevent overcharge and decomposition of the Rapamycin.

Results and discussion

Grain boundary etching

Etching 10 min with a current of 100 mA (1.14 mA/mm^2) produced a surface with ~5 μm wide furrows of up to 5 μm depth around the grains (Rz = 9.8 μm) (Fig. 2). The furrow depth was measured by SEM analysis of a polished section. Applying a current of 200 mA (2.28 mA/mm^2) for 10 min produced a very rough (Rz = 15.8 μm), granulated surface (Fig. 3). In order to get detailed information about the selectivity of the etching process in dependence of the applied current, polished sections were made of stents etched with different currents and etching times. The parameters were chosen in a way that the furrow depth is smaller than half the grain perimeter, so that detachment of grains is avoided. From each stent strut the average length of the five longest crevices were measured, as well as the thickness loss of the strut. The ratio of the average of the furrow depth plus the thickness loss to the thickness loss was regarded as an index for the selectivity of the etching process. Interestingly it was found that the selectivity does not vary significantly (Fig. 4) within the measured range of 50 mA (0.57 mA/mm^2) to 800 mA (9.12 mA/mm^2). This observation is in contrast to former grain boundary etching models where the U/I curve of grain boundaries and matrix is assumed as illustrated in Fig. 1. According to this model a high selectivity could only be achieved in a small range of voltage, where the current curve has a high slope. This

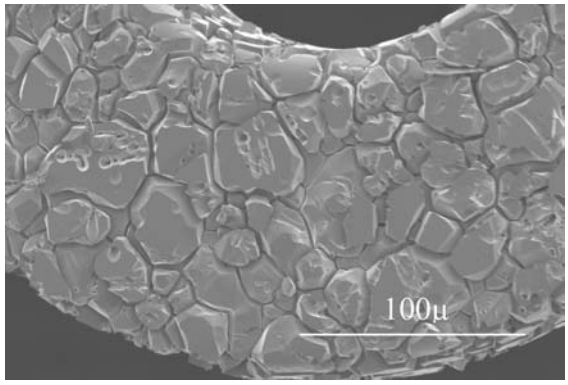

Fig. 2 Grain boundary etched stent, 500× surface (10 min, 1.14 mA/mm^2)

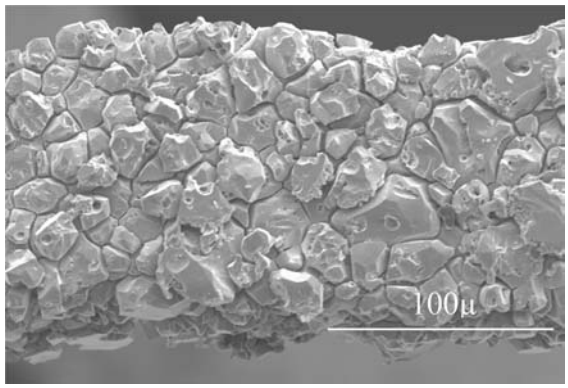

Fig. 3 Grain boundary etched stent surface, 500× (10 min, 2.28 mA/mm^2)

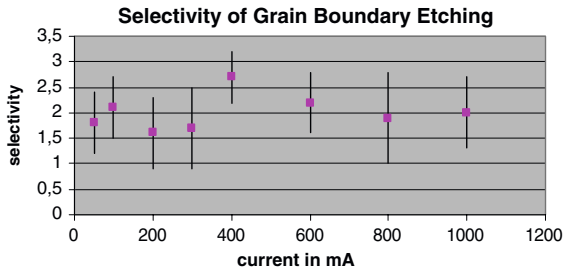

Fig. 4 Selectivity of grain boundary etching, measured on cross sectional micrographs

area is marked as the ''grain boundary etching range'' in the diagram. At high currents the selectivity would drop to very low values. In order to verify the congruence between the model and the measured speciments a U/I diagram of one of the analysed samples in nitric acid was measured (Fig. 5). Besides a slight current increase in the equilibrium potential area it is almost identical with the curve in Fig. 1. The initial current increase can be explained with slight decomposition reactions of the nitric acid.

A surface of the heavily etched type (200 mA) has been measured by laser topography. Calculating the theoretical storage volume offered by the furrows between the grains rendered a value of 0.146 mm^3/cm^2, corresponding to ~2 µg Rapamycin/mm^2 stent surface. Due to the stent being etched on a pin, the inner side of the stent struts is largely spared by the etch attack (see Fig. 6). This means a welcome side-effect of the etching methods. The inner part is in contact with the catheter balloon during dilatation and therefore a rather smooth inner surface is desired to avoid balloon damage.

Coating behaviour of grain boundary etched stents and quantification

The amount of drug on the coated stent was determined to 36.6 µg/mm^2 (versus electropolished: 21.4 µg/mm^2) (n = 3) after dilatation. SEM Analysis showed an evenly

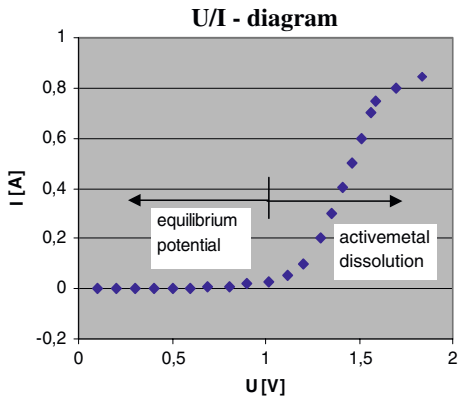

Fig. 5 U/I-diagram of 316L of the analysed specimens

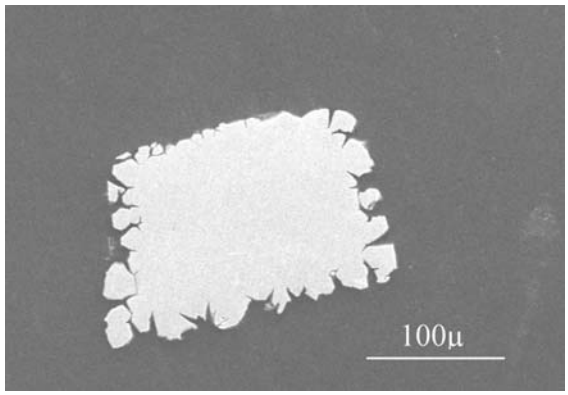

Fig. 6 Grain boundary etched surface, 400× (10 min, 2.28 mA/mm^2), cross sectional micrograph of a single strut

covered, smooth surface with the Rapamycin being absorbed by the microstructure (see Figs. 7 and 8). In comparison to electropolished stents (Figs. 9 and 10) markedly less flaking was observed after dilatation. Flaking of the drug layer may, on the one hand, lead to a thrombosis risk, on the other hand it indicates insufficient adhesion properties. Only at the areas of high stress, namely at the bends little cracks can be found (see Fig. 8).

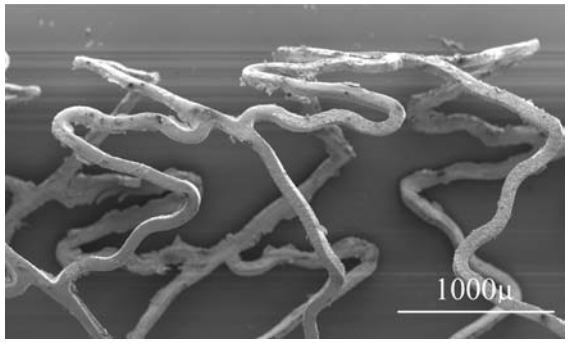

Fig. 7 Grain boundary etched stent surface, 20× (10 min, 1.14 mA/mm^2) coated with 2% Rapamycin solution after dilatation

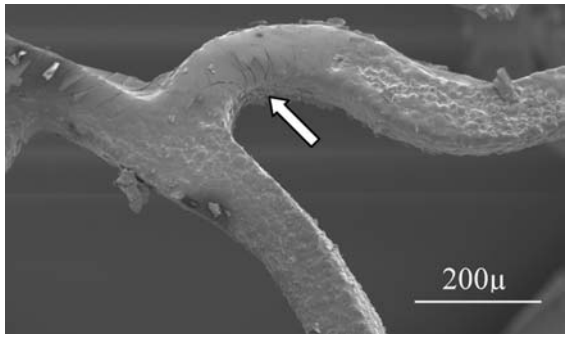

Fig. 8 Grain boundary etched stent surface, 100× (10 min, 1.14 mA/mm^2) coated with 2% Rapamycin solution after dilatation

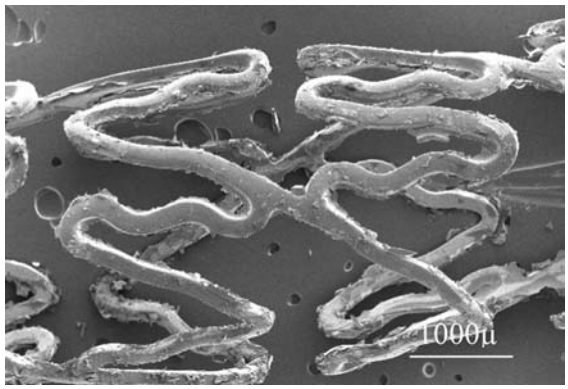

Fig. 9 Electropolished stent coated with 2% Rapamycin solution after dilatation, 30×

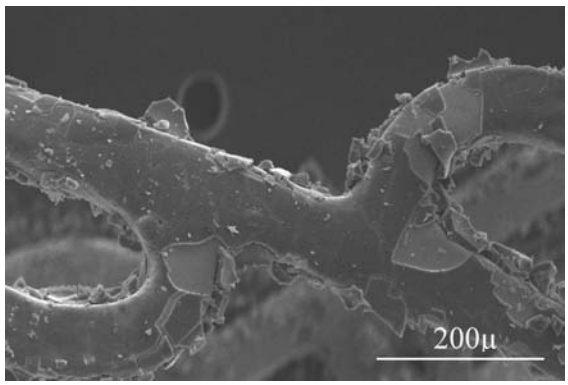

Fig. 10 Electropolished stent coated with 2% Rapamycin solution after dilatation, 100×

Adhesion tests yielded 21% drug loss during implantation (vs. 24 % for electropolished stents) (n = 3).

Hydrochloric acid etching

An etching procedure of 10 min at a current of 2.28 mA/mm^2 in stirred (300 rpm) etching solution, produced an evenly rough, terraced surface (Figs. 11 and 12). Roughness values were determined as Ra = 0.51 ± 0.14 µm (Rz = 3.29 ± 0.84 µm) (n = 9). It was found that the result

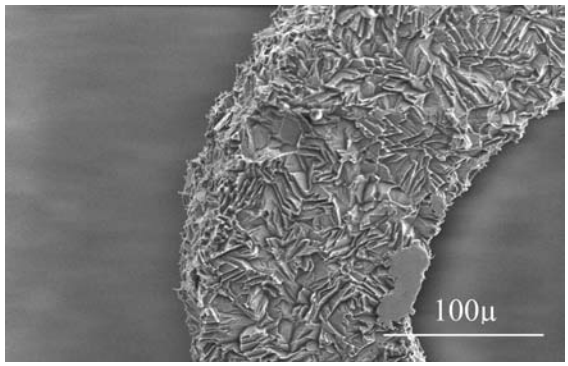

Fig. 11 Chloride etched stent surface, 400× (10 min, 2.28 mA/mm^2)

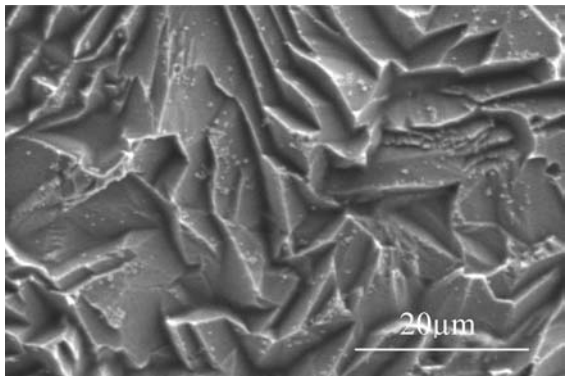

Fig. 12 Detail chloride etched stent surface, 2000× (10 min, 2.28 mA/mm^2)

of this etching method is strongly dependent on a tight contact between stent and pin. Poor contact results in the formation of a thin interface layer probably consisting of metal oxides and hydroxides between stent and pin, preventing proper etching of the stent.

An examination of the initial phase of this etching method (Figs. 13 and 14) shows the creation of evenly distributed small pits of different geometries that become visible at high magnifications (marked with black arrows in Fig. 14). As described in [7] on p. 194 triangular pits

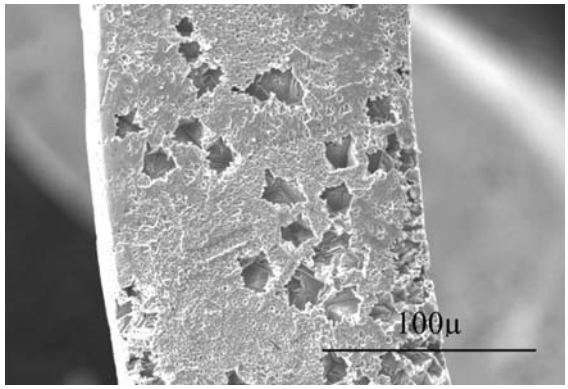

Fig. 13 Chloride etched stent surface, 500× (5 min, 2.28 mA/mm^2)

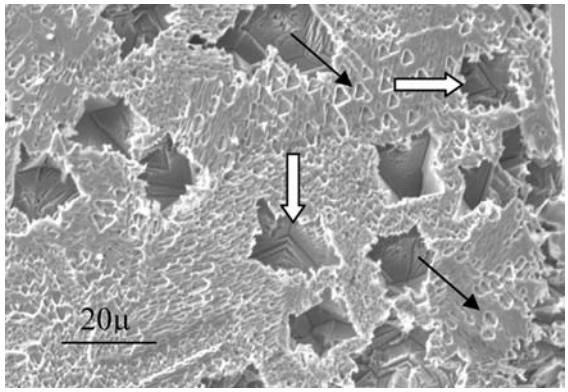

Fig. 14 Chloride etched stent surface, 1000× (5 min, 2.28 mA/mm^2)

suggest that the attacked surface is orientated in the (111) direction whereas rectangular pits are created at (110) planes. Some of the pits have progressed to holes of several μm size which show a platelet-like surface inside (marked in Fig. 14 with white arrows). Several factors may be responsible for this form of corrosion. Firstly as a result of high mechanical strain during the processing of the tubes a high dislocation density is present, enabling the formation of a high number of evenly distributed small pits. Secondly the effect of the stirrer prevents the formation of a consistent etch film on the surface so that the electropolishing effect is suppressed. Furthermore no protecting passivity layer can be maintained over the growing pits as it is the case in pitting corrosion [10]. Because of these factors no growing hemispheres with smooth inner surfaces can develop. Instead a selective etch attack takes place, which, in the initial phase, creates small triangular or rectangular pits. Where the surface is etched further it shows platelet-like appearance according to the orientation of the grains. While the high amount of pits prevent the inhomogeneous growth of single pits and a uniform terraced surface is created.

Coating behaviour of hydrochloric acid etched stents and adhesion tests

The amount of drug on the coated stent was determined to 27.7 μg/mm^2 (versus electropolished: 21.4 μg/mm^2) (n = 3) after dilatation. A smooth, even drug film (Figs. 15 and 16) could be observed under SEM. Similar to the grain boundary etched surfaces only little flaking of the drug layer can be found. Similar to the coated grain boundary etched stents some minor cracks can be found at the bends (see Fig. 16). Adhesion tests however yielded 51% drug loss during implantation (vs. 24% for electropolished stents) (n = 3). This unexpected result indicates that the terraced surface might weaken the integrity of the drug layer by providing sharp edges that act as crack initiators.

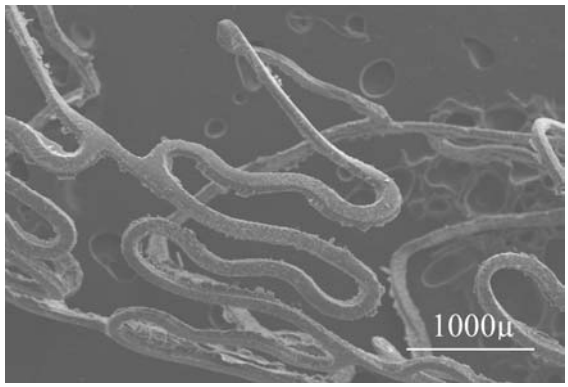

Fig. 15 Chloride etched stent surface, 20× (10 min, 2.28 mA/mm^2) coated with 2% Rapamycin solution after dilatation

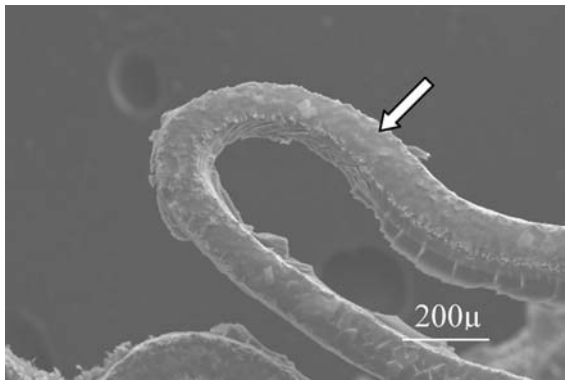

Fig. 16 Chloride etched stent surface, 100× (10 min, 2.28 mA/mm^2) coated with 2% Rapamycin solution after dilatation

Summary

Two methods of electrochemical surface microstructuring as a basis for drug-coating of coronary stents have been evaluated. The basic approach of this work is to use electrochemical etching techniques in which the intrinsic material structures are used to create randomly distributed microstructures. In contrast to mechanical roughening procedures the surfaces can be created without mechanical strains. Both etching techniques offer the possibility of creating microstructured implant surfaces as a basis for drug coatings. The aim is to increase both the drug amount on the surface and the adhesion of the drug. Electrochemical etching with hydrochloric acid at 2.28 mA/mm^2 produced an evenly rough, terraced surface. Adhesion tests indicate that, against the assumptions, this surface did rather deteriorate the adhesion properties than improving it. Electrochemical grain-boundary etching rendered a furrowed, microstructured surface offering volume for the coating drug. Interestingly a broad range of high selectivity was found (at current densities between 0.57 and 9.12 mA/mm^2) instead of a limited range of high selectivity as described in literature [9]. It could be shown that etching stents with the grain boundary etching method resulted in a higher amount of drug on the stent after dilatation with at least equal coating adhesion compared to electropolished stents. An analysis of the in vitro release kinetics as well as the mechanical and chemical stability of the etched stents will be subject of further investigations.

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