Parylene N coating on stainless steel surface as a protective layer for metal implants

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The protection properties of parylene coating on implant stainless steel 316L was investigated. The electrochemical measurements and metal ions release tests in Hanks solution revealed that the coating can be successfully used for corrosion protection. The addition of hydrogen peroxide, simulating the inflammatory response of human body causes a decrease of protection properties of the coating. However, usage of parylene coating on stainless steel reduce iron ions release rates.

Keywords and phrases: stainless steel, implantable material, polymer protective coating, parylene.

Introduction
Stainless steel (SS) is a widely used orthopedic implant material for internal fixation. Its mechanical strength, low cost and the capability to bend and shape the implant to create a custom fit in the operating room makes the material strongly competitive to titanium. However, upon prolonged contact with body fluids, corrosion phenomena takes place resulting in a high rate of systemically released metal corrosion products [1, 2]. This corrosion and release of ions may lead not only to mechanical failure of implant but also to local pain and swelling in the near implant region. The presence of metal ions in the organism causes the histopathological changes in detoxication organs (liver, kidney, spleen) and even induction of tumours. Therefore, emphasis is being put on elaborating a barrier against heavy metal ion release to the human body. Many examples are described of investigations on metal implants covered by different coatings. While polymer coatings for surface modification and protection are widely used in different manufacturing applications, this kind of material is also used as a coating for medical devices. One of the polymers that draws the most attention for medical devices nowadays is parylene N (poly-para-xylylene), which has excellent biocompatibility and capability to form a thin uniform film. A crystal-clear parylene layer, which can be easily vacuum-deposited, has a very low potential for triggering an immune response and is highly resistant to corrosive conditions of body fluids environment. The film also forms an effective barrier against channeling of contaminants from a coated surface to the surrounding [3].

Most investigations on coatings used for medical devices aim at increasing the corrosion resistance of metal implants. Corrosion resistance and biocompatibility are the two fundamental properties of metal implants. At the same time, these properties determine the interaction between the metal surface and human body to from an electrochemical and a biological point of view. The electrochemical methods are generally used for monitoring the processes taking place on metal implant surfaces in artificial biological environments. To simulate inflammatory reactions caused by implanted foreign object in a human body, an artificial body fluids with addition of hydrogen peroxide is used for in vitro studies [4]. These kinds of experiments, involving electrochemical measurements, are in good agreement with their biocompatibility response obtained from in vivo experiments [5].

Aim of this paper is to report on examination of the protective properties of parylene N coating on stainless steel surface against a corrosion process.

Experimental
Test materials
Samples of SS 316L grade (Table 1), cold rolled and bright annealed (BA) surface finishing, were supplied by Swerea KIMAB AB. Prior to the analysis, samples were cut in square-shaped coupons of 20 × 20 mm² (0,8 mm).
The surface of the samples were cleaned and pickled and some of them were coated with a 2 μm layer of parylene N via chemical vapor deposition (CVD) by Para Tech Coating Scandinavia AB as seen in Fig. 1.

Prior to electrochemical analysis, the coated and the uncoated samples were cleaned in three steps, first with acetone, then with ethanol and finally with distilled water and then the samples were dried in air.

Before metal ions release tests, all the samples were cleaned in 2% RBS® (an alkaline detergent containing anionic, cationic and non-ionic surface-active agents without phosphates) for 10 min at 50°C ± 2°C to remove any organic residues from the surface. After cleaning, the samples were immersed in ultra pure water for 3 minutes, rinsing with ultra pure water and finally dried with air at room-temperature.

Exposure conditions
All electrochemical investigations and metal ions release tests were performed in Hanks solution and Hanks solution with 100 mM hydrogen peroxide. In the experiments, the commercial Hanks solution (pH = 7.4) of Aldrich analytical grade was used. Hanks solution is an artificial salts mixture usually used in combination with naturally occurring body substances (blood serum, tissue extracts) and/or more complex chemically defined nutritive solutions for culturing animal cells. In the experiments, the commercial Hanks solution (pH = 7.4) of Aldrich analytical grade was used. Addition of H2O2 is used to simulate certain reactions, which take place when a foreign object enters a human body. H2O2 is also the product of the biochemical reactions continuously taking place in the human body.

To ensure the reliability of the low concentration metal analysis, all the vessels used for the metal release experiments were cleaned with 10% HNO3 for 30 h and then rinsed in ultra pure water to remove any metal-containing contaminants.

Samples were placed in the vessels with 8 mL of Hanks solution. Immersion experiments were performed for 28 days in darkness using a shaking water bath at a temperature of 37°C. Reference vessels, containing fluid without SS samples, were also treated under the same conditions.

Methods
The electrochemical impedance spectroscopy (EIS) measurements were performed using a typical three electrode set-up describe in detail elsewhere [6]. Three-electrode electrochemical cell used consists of a sample work electrode, a Pt mesh counter electrode and a saturated K/KCl reference electrode. The electrodes were connected to a 1287 Electrochemical Interface coupled with a Solartron 1250 Frequency Response Analyzer. A computer with CorrWare and ZPlot Software was used for data acquisition and analysis. During the experiments, the exposed sample area was 1 cm². The measurements were performed using 250 mL solution at room temperature in ambient condition. Prior to the EIS measurement, the OCP was recorded for 1 hour to ensure a stable potential of the sample. The EIS measurement was performed at the OCP and repeated after 1 hour, to monitor the changes in the coated sample, i.e., changes occurring in the coating and at the interface between the stainless steel and the coating. The impedance spectra of the samples were analyzed in Nyquist and Bode plots.

Samples of the solution after the 28-days exposure period of stainless steel to the Hanks solution and Hanks solution with hydrogen peroxide were analyzed for the concentrations of the released metals (Fe, Cr, Ni). The Atomic Absorption Spectrometer Perkin-Elmer Model 3110 (with graphite furnace HGA-600) and Perkin Elmer type 4100 ZL instruments were used. The detection limits were 3, 2, 4 ng/ml (FAAS) and 0.02, 0.01, 0.1 ng/ml (ETAAS) for Fe, Cr and Ni, respectively.

Results and Discussion
The EIS results were interpreted in terms of a Nyquist Plots (Fig. 2a), which presented the typical spectra for

| Table 1. Elemental composition of the 316 grade of stainless steels. |
|-------------------|---|---|---|---|---|---|---|---|---|---|
| Fe    | C    | Cr    | Ni    | Mo    | Mn    | Si    | S    | P    | N    |
| min   | balance |     | 16.0  | 10.0  | 2.0   | –     | –    | –    | –    |
| max   | 0.08  | 18.0  | 14.0  | 3.0   | 2.0   | 0.75  | 0.03 | 0.045| 0.1  |

| Table 2. Chemical composition of Hanks solution. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| NaCl            | CaCl₂           | MgSO₄ *H₂O      | KCl             | KH₂PO₄          | NaHCO₃          | Na₂HPO₄ *2H₂O   | Glucose         | Distilled water |
| 0.8 g           | 0.02 g          | 0.02 g          | 0.04 g          | 0.01 g          | 0.127 g         | 0.01 g          | 0.2 g           | 100 ml          |
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uncoated SS samples exposed to Hanks solution and Hanks solution with H$_2$O$_2$.

The obtained Nyquist plots are not semicircles but rather only a parts of an arcs of a semicircles with the centre below the x-axis. This behaviour can be described by the model of the interface with one resistance (Rp), representing the resistance to charge transfer over the interface in parallel to capacitor (C1), representing the double layer capacitance. In non ideal model, when real surface has heterogeneous properties, the capacitive behaviour of the double layer is often described by Constant Phase Element (CPE). For electrochemical measurements, the resistance of the electrolyte (Rs) is added in series to the interfacial model [7].

The simplest equivalent model, characterized for a one time constant evident, fitted to data of uncoated sample is shown in Fig. 3.

![Fig. 3. Equivalent electrical model used to fit data for uncoated SS samples exposed to Hanks solutions.](image)

The same equivalent circuit can be used for fitting the data of uncoated sample exposed to Hanks solution and Hanks solution with H$_2$O$_2$. The addition of hydrogen peroxide to the Hanks solution slightly changes the results in the EIS spectra. For the uncoated samples exposed to this solution, a smaller semicircle was observed indicating that the sample surface is less resistant to corrosion processes.

At Fig. 2b, the EIS results from the parylene coated samples exposed to Hanks solution and Hanks solution with the H$_2$O$_2$ addition are shown. In both experiments, a straight line on the Nyquist plots revealed the same electrochemical characteristics. This linear trend indicates a high impedance value characteristic for a good barrier coating on the steel. It implies that, in both solutions, the polymer coating correspond to an isolating material, effectively protecting the steel surface during the entire period of taking measurements. Therefore, in this case it’s impossible to use any equivalent circuit for fitting the data of parylene samples exposed to Hanks solution and Hanks solution with H$_2$O$_2$.

The amount of released Fe, Cr and Ni ions from uncoated and parylene coated stainless steel grade 316L samples to the Hanks solutions are presented Fig. 4.

In general, it can be noted that iron is preferentially released from all the samples. The release rates of nickel and chromium ions, from uncoated and coated samples, to Hanks solution are practically within the detection limit.

In the case of exposure to Hanks solution with H$_2$O$_2$, the quantity of metal ions released is one (or more) order of magnitude higher. The results of release tests to Hanks solution with hydrogen peroxide show that, after a month of exposure, the amount of ions released from parylene coated SS samples is lower than for uncoated samples. Usage of the layer of 2 μm of parylene coating reduced 4 times the iron ions release rates to Hanks solution with H$_2$O$_2$, what is extremely important specially for medical applications.
Conclusion

In general, it can be concluded that parylene N can be used as a protective polymer on SS surfaces used for biomedical applications. A good adhesive and isolating properties (revealed by electrochemical measurements) makes the parylene N a suitable protective material against both surface corrosion and heavy metal ions release to the organism.

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References


Fig. 4. Metal ions release rates for uncoated and parylene coated samples exposed to a) and b) Hanks solution, c) and d) to Hanks solution with H₂O₂ after 28 days.