Microelectrochemical characterization of titanium biomaterials by scanning electrochemical microscopy

Doctoral thesis

Ph.D.

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1. Introduction

Titanium and its alloys are of particular interest for biomedical applications. They have been widely used for clinical applications such as dental implants, stents, and orthopedic devices because of their exceptional biocompatibility and their outstanding mechanical properties such as low elastic modulus, high tensile strength, and low density. Also, they are known for their exceptional osseointegration character functioning in living tissue. Besides, they are well known for the high resistance to corrosion that is provided by the robust protective film formed on titanium surface which inhibits the release of metal cations from the surface and hinders the electron transfer reactions with the surrounding environment. However, the clinical failure cases of titanium and its alloys were intensively reported. The release of metal ions from the implanted titanium biomaterials was detected in blood and urine, on the other hand, localized corrosion was observed in vitro and in vivo. While in the human body the implanted biomaterials can undergo corrosion via chemical, biological, and mechanical impacts. Fundamentally, the localized corrosion can take place if a damaged passive film required a longer time to be completely healed. Thus, the corrosive species in the electrolyte will enhance the corrosion of the metal that leads to the nucleation of non-propagation pits. That results in the occurrence of localized corrosion. Therefore, the study of the self-healing kinetics of the passive film on titanium biomaterial is crucial.

As commonly known, the implanted biomaterials are highly prone to fretting corrosion. That is the result of the micromovement generated between the implant and the adjacent bone or metal surface. Several studies examined the fretting corrosion of different titanium alloys. It was proved that it rises the corrosion of titanium and its alloys. Besides, it was demonstrated that it affects the electrochemical potential of titanium biomaterials. Despite this, their electrochemical potential can shift to a lower value as low as -1500 mV. Moreover, numerous reports showed that the cells around the titanium implant decline with the increase of the negative polarization. Therefore, understanding the electrochemical properties of titanium under the cathodic polarization in situ is highly demanded.

Nitinol that is an equiatomic alloy of nickel and titanium regarded among the most useful biomaterial in the field of health care. However, its clinical application problems were broadly reported such as the release of nickel ions from Nitinol biomaterial exposed to the neutral physiological medium. That was suggested to be as a result of the nickel ions released from areas enriched with nickel on the Nitinol surface. Also, the release of titanium ions accompanied by an intensive release of nickel was detected from Nitinol soaked in the acidic

physiological medium. However, the source of titanium still regarded as an enigma. Thus, a deep understanding of the corrosion of Nitinol in the acidic medium regarded as crucial issue.

Another clinical problem related to Nitinol is its susceptibility of undergoing pitting corrosion that was verified in vivo. It was confirmed too by several electrochemical testing methods such as potentiodynamic polarization and SECM. However, no systematic study has been carried out to monitor the corrosion products that evolve during the corrosion of Nitinol.

2. Aims

The major aim of my experimental work was to gather in situ information about the electrochemical behavior of titanium biomaterials (pure titanium, titanium G4, and Nitinol) exposed to different conditions.

My target subfields were as follow:

- The investigation of the kinetic and the corrosion mechanism of the self-healing process of the passive titanium film on titanium G4 surface.
- Examination of the cathodic polarization impact on the electron transfer reaction on titanium biomaterial surface.
- Investigation of the corrosion on the Nitinol biomaterial in the acidic medium.
- Monitoring the corrosion products evolve during the corrosion of the Nitinol biomaterial.

3. Methods

In my experimental work scanning electrochemical microscopy technique was proposed. That is considered a powerful in situ tool for understanding the electrochemical properties of metal surfaces. Also, conventional electrochemical techniques were employed such as electrochemical impedance spectroscopy and potentiodynamic polarization techniques. Also, to detect the release of the metal cations the atomic absorption spectroscopy was employed.

4. Results

In my dissertation, the properties of different titanium samples were investigated such as pure titanium, titanium G4, and Nitinol. Their properties were examined in different conditions. While a new transient event was observed that must be considered for their clinical application. The obtained results are summarized as follow:

- The electrochemical reactivity of the titanium G4 implant surface after the removal of the passive film has been investigated using SECM operated in the amperometric mode. It was found that several minutes are needed for the formation of a compact passive film on the titanium G4 surface.
- Using the SECM in the potentiometric mode via employing antimony as SECM probe, the corrosion mechanisms of the passive film on titanium G4 were investigated. After the mechanical removal of the protective film, acidification was sensed at the vicinity of titanium G4 implant surface. That indicated the release of titanium cations from the implant surface. Thus, the self-healing is a critical factor that must be considered for the biomaterial application because longer healing time would enhance the corrosion of the implanted biomaterials. That may lead to reduce mechanical properties of the implant. Also, longer healing time would affect the viability of the cells around the implanted biomaterial.
- Using SECM operated in the feedback mode, the electrochemical properties of the commercial titanium biomaterial under the cathodic polarization has been studied. It was demonstrated that the increase of the cathodic polarization enhances the electron transfer reaction at the titanium oxide/electrolyte interface. This can arise as a straight forward explanation of the decrease of the viability of the biological cells under cathodic polarization reported in the literature.
- The corrosion products that evolve during the corrosion of Nitinol were successfully investigated. Using SECM operated in the amperometric mode anodic and cathodic spots were detected. Besides, via using antimony microelectrode as an SECM probe acidification and alkalization were detected in the anodic and cathodic spots, respectively
- The corrosion of the Nitinol biomaterial was investigated in neutral and acidic 0.1M NaCl. While at neutral 0.1M NaCl the passive film on the Nitinol biomaterial stays in a passive state. However, at acidic pH close to inflammatory condition that is about pH=3, the transpassivation of the passive film on Nitinol biomaterial was observed. Trying to understand the nature of the transpassivation event the occurrence of the electron transfer reaction between Nitinol and the surrounding environment was found experimentally. Also, the interaction was proved by finding intensive release of hazardous nickel ions at the early stage of the immersion of Nitinol at the acidic 0.1M NaCl. Furthermore, it was demonstrated that tens of minutes are required for the formation of the compact passive film on the Nitinol after the acidic attack.

5. Thesis points

The work presented in my thesis devoted to the electrochemical characterization of the titanium biomaterials using scanning electrochemical microscopy. Aimed to understand their electrochemical properties and draw attention to new transient events that must be considered for their application. The obtained results are summarized below:

- Thesis point 1 :

The mechanical impact on the electrochemical reactivity of the titanium G4 implant surface has been investigated using SECM operated in amperometric mode. It was found that the kinetic of the self-healing of the protective film on the titanium surface is a time dependent process, several minutes needed for the formation of a compact film.

- Thesis point 2 :

The corrosion mechanisms of the passive titanium dioxide were studied using the SECM in potentiometric mode. Antimony microelectrode was used as SECM probe, while acidification was sensed at the vicinity of the mechanical damaged titanium G4 implant surface. It indicates the discharge of the titanium cations from the implant surface. Therefore, care must be taken for minimizing the time of the self-healing process because longer healing time would enhance the corrosion of the implanted material that causes a discharge of hazardous metal cations. That may lead to reduce the mechanical propertied of the implant.

- Thesis point 3 :

Cathodic polarization on the electrochemical properties of the passive film formed on commercial pure titanium has been studied. Using SECM operated in the amperometric mode it was demonstrated that the anticorrosion property of the protective film decreases with the increase of the cathodic polarization. That was proved by the occurrence of the electron transfer reaction at the titanium oxide/electrolyte interface. This can arise as a straight forward explanation of the decrease of the viability of the biological cells under cathodic polarization reported in the literature.

- Thesis point 4 :

The change of the titanium behavior from passive to conductive under cathodic polarization was explained by the hydrogen intercalation into the titanium oxide film, hydrogen acting as a doping element.

- Thesis point 5 :

The corrosion of the anodically treated Nitinol was examined. Using SECM in the amperometric mode, anodic and cathodic sports were visualized. While redox competitive effect was observed in the anodic areas, on the other hand, positive feedback occurs at the cathodic spots. Furthermore, employing antimony as SECM tip acidification and alkalization processes were detected in the anodic and cathodic areas, respectively.

- Thesis point 6 :

The effect of acidic medium on the electrochemical properties of the Nitinol surface was investigated. It was demonstrated that at pH close to the normal physiological condition that is about 7, the spontaneously formed passive film on Nitinol stays in passive state. However, at pH-s adjacent to inflammatory condition that is about pH=3, the passive film on Nitinol surface breaks down. It was proved by the occurrence of the electron transfer reaction between Nitinol and the surrounding environment. That is due to the formation of pits on the surface caused by the nickel oxide dissolution. It was confirmed too by the significant discharge of hazardous nickel ions soon after exposure of Nitinol to the acidic solution. Furthermore, it was shown that tens of minutes are required for the total repassivation of the Nitinol upon the acidic attack. Hence, the surface treatment of the Nitinol regarded as critical toward reduce the nickel amount on the Nitinol surface.

6. Publications

Publications forming the basis of PhD dissertation:

[1] **A. Asserghine**, M. Medvidović-Kosanović, L. Nagy, G. Nagy, *In Situ Monitoring of the Transpassivation and Repassivation of the Passive Film on Nitinol Biomaterial by Scanning Electrochemical Microscopy*, ***Electrochemistry Communications*** 107 (2019), 106539.
(IF : 4.19, Q1)

[2] **A. Asserghine**, D. Filotás, B. Németh, L. Nagy, G. Nagy, *Potentiometric Scanning Electrochemical Microscopy for Monitoring the pH Distribution During the Self-Healing of Passive Titanium Dioxide Layer on Titanium Dental Root Implant Exposed to Physiological Buffered (PBS) Medium*, ***Electrochemistry Communications*** 95 (2018), 1-4.
(IF : 4.66, Q1)

[3] **A. Asserghine**, D. Filotás, L. Nagy, G. Nagy, *Scanning Electrochemical Microscopy Investigation of the Rate of Formation of a Passivating TiO_2 Layer on a Ti G4 Dental Implant*, ***Electrochemistry Communications*** 83 (2017) 33-35.
(IF : 4.56, Q1)

[4] **A. Asserghine**, M. Medvidović-Kosanović, A. Stanković, L. Nagy, R. M. Souto, G. Nagy, *Sensing the Localized Corrosion Reactions at Anodically Degradable Nitinol Biomaterial by Scanning Electrochemical Microscopy*, Under preparation.

[5] **A. Asserghine**, M. Medvidović-Kosanović, L. Nagy, R. M. Souto, G. Nagy, *Scanning Electrochemical Microscopy Investigation of the Cathodic Polarization Impact on the Electrochemical Behavior of Titanium Biomaterial*, Under preparation.

Other publications:

[1] Z. Meiszterics, **A. Asserghine**, A. Kiss, L. Nagy, T. Zsebe, G. Nagy, *Potentiometric Scanning Electrochemical Microscopy (SECM) investigation of 3D printed parts produced by CMT Welding Technology*, Accepted in **Electroanalysis** (2020).
(IF : 2.67, Q2)

[2] A. Stanković, Ž. Kajinić, J. V. Turkalj, Ž. Romić, M. D. Sikirić, **A. Asserghine**, G. Nagy, M. Medvidović-Kosanović, *Voltammetric Determination of Arsenic with Modified Glassy Carbon Electrode*. Accepted in **Electroanalysis** (2020).
(IF : 2.67, Q2)

[3] D. Filotás, **A. Asserghine**, L. Nagy, G. Nagy, *Short-Term Influence of Interfering Ion Activity Change on Ion-Selective Micropipette Electrode Potential; Another Factor that can Affect the Time Needed for Imaging in Potentiometric SECM*, **Electrochemistry Communications** 77 (2017) 62-64.
(IF : 4.56, Q1)

7. Conference presentations

Oral presentations :

[1] A. Asserghine, L. Nagy, G. Nagy, *Electrochemical Characterization of Titanium and its Alloys Assessed by Scanning Electrochemical Microscopy in Amperometric and Potentiometric Modes*, 10th Workshop on Scanning Electrochemical Microscopy (SECM-10), Paris, France, 2019.

[2] A. Asserghine, D. Filotás, M. L. Nagy, G. Nagy, *Electrochemical Characterization of Titanium Biomaterials Using Scanning Electrochemical Microscopy*, Analytical days, Balaton, Hungary, 2018. "Best oral presentation winner"

[3] A. Asserghine, D. Filotás, M. L. Nagy, G. Nagy, *Electrochemical Characterization of Titanium Biomaterials Using Scanning Electrochemical Microscopy*, 1st Cross-Border Seminar on Electroanalytical Chemistry, Furth in Wald, Germany, 2018.

[4] A. Asserghine, D. Filotás, L. Nagy, G. Nagy, *Scanning Electrochemical Microscopy Investigation of the Rate of Formation of a Passivating TiO_2 Layer on a Ti G4 Dental Implant*, 9th Workshop on Scanning Electrochemical Microscopy (SECM-9), Warsaw, Poland 2017.

Poster presentations :

[1] A. Asserghine, L. Nagy, G. Nagy, *In Situ Monitoring of the Transpassivation and Repassivation of the Passive Film on Nitinol Biomaterial by Scanning Electrochemical Microscopy*, International Conference on Chemical Sensors, Visegrád, Hungary, 2019.

[2] D. Filotás **A. Asserghine**, L. Nagy, G. Nagy, *Short-Term Influence of Interfering Ion Activity Change on Ion-Selective Micropipette Electrode Potential; Another Factor that can Affect the Time Needed for Imaging in Potentiometric SECM*, International Conference on Electrochemical Sensors, Visegrád, Hungary, 2017.