Coatings based on natural polymers on Ti15Mo alloy for medical applications

Continuous progress in the field of implantology is inevitably associated with an increase in the demand for new materials and the development of surface engineering technology. So far, non-metallic materials meeting the required technological and strength criteria have not been developed yet, which is why the implants are still entirely or partly made of metal alloys. The research conducted in the doctoral thesis focuses on the surface engineering of metallic biomaterials belonging to the latest generation of nickel-free titanium alloys. Bearing in mind the ever increasing number of implant treatments and numerous literature reports on the impact of the surface layer of metallic biomaterials on tissue integration, this thesis attempts to functionalize the Ti15Mo titanium alloy surface by passivation and electrophoretic deposition of natural polymers like alginate, hyaluronate and chitosan.

In the first part of the work, the physical and chemical properties and corrosion resistance of the Ti15Mo alloy in the initial state were determined. The conducted electrochemical tests indicated excellent corrosion resistance of the innovative Ti15Mo alloy in conditions imitating the human body environment in both long- and short-term research, and the results clearly indicate the possibility of using the Ti15Mo alloy for short- and long-term implants. In addition, the analysis of EIS results revealed the two-layered nature of the oxide structure formed under the influence of the human body environment. Resulted oxide layer is composed of a compact inner barrier layer and an outer porous one. The influence of the passivation type of Ti15Mo alloy surface on its corrosion resistance in the environment of simulated body fluids was also determined. The modification of the surface of the Ti15Mo alloy by means of various passivation methods increases its corrosion resistance and allows to obtain a thicker oxide layer.

In the second part of the work, in order to improve the biocompatibility and bioactivity of the obtained biomaterials, coatings from natural polymers such as chitosan, hyaluronan and alginate were formed on Ti15Mo surface by electrophoretic deposition. During the research, an electrophoretic deposition method was developed which allows for more efficient deposition of anionic polymers through the use of ZnO interlayer. This method has been published and forms the basis of patent application No. P.407556. "Method for the deposition of a bioactive coating of anionic natural polymer in the form of alginate or hyaluronan on a titanium alloy element". The attempts of co-deposition of composite coatings of zinc oxide nanopowder with hyaluronan and chitosan have been also made.

The kinetics of the electrophoretic process of deposition of biopolymer coatings on the Ti15Mo alloy and the influence of process conditions such as time, tension and composition and concentration of the deposition bath on process efficiency as well as the thickness and morphology of the obtained coatings were determined during the tests. The obtained biomaterials were subjected to a series of structural, physicochemical, electrochemical, biological and micromechanical tests to enable characterization of the modified surface of the metallic implant material. Corrosion resistance of the obtained coatings was examined by classical electrochemical methods, as well as an innovative method of electrochemical impedance spectroscopy, which allowed to determine the corrosion behavior and the degree of water absorption in the obtained polymer coatings. In cooperation with the Foundation of Cardiac Surgery in Zabrze, the biocompatibility of the obtained biomaterials was assessed. Assessment of in vitro corrosion resistance of Ti15Mo alloy with deposited biopolymer coatings showed its improvement as a result of the use of alginate and hyaluronate coatings. Impedance tests of polymer coatings have shown a gradual decrease in their corrosion resistance as the immersion time in the saline solution increases as a result of the absorption of water leading to an increase in the contact surface of the substrate with the electrolyte. Evaluation of in vitro compatibility of deposited coatings has shown that in the case of hyaluronan and alginate coatings, hemolysis and their toxicity to fibroblasts are not observed. However, cytotoxicity studies revealed a negative effect of chitosan coatings on fibroblast cultures.

The developed technology for the modification of the implant surface of the Ti15Mo alloy is currently at the IV level of TRL technology readiness and encourages for further research.