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Corrosion behavior of PEO coatings with Mn_3O_4 on Mg-Zn-Ca alloys in inflammatory conditions

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INTRODUCTION: The inflammatory response triggered by orthopedic devices results in the generation of reactive oxygen species (ROS) and a decrease in pH, accelerating the corrosion rate of Mg implants. To address corrosion challenges, various strategies are explored, including alloying with zinc and calcium elements and surface modifications. Plasma electrolytic oxidation (PEO) emerges as a promising technology, forming porous MgO coatings on Mg surfaces [1]. The electrolyte composition and the incorporation of additives not only affect coating characteristics but also influence the thickness and porosity of PEO coatings, collectively playing crucial roles in determining and preventing corrosion [2]. This study underscores the potential use of additives with ROS-scavenging properties, such as manganese-based additives in the PEO electrolyte, and the synthesis of MgO-Mn_3O_4 coatings on Mg-Zn-Ca alloy, as a means to mitigate corrosion rates, especially in inflammatory conditions.

EXPERIMENTAL: In this study, PEO coatings incorporating Mn_3O_4 were fabricated on Mg-Zn-Ca substrate using two distinct methods: the introduction of $KMnO_4$ salt and the inclusion of Mn_3O_4 nanoparticles in the electrolyte composition. In the first approach, composite coatings were chemically synthesized within the plasma microdischarge area, while the second route involved physical processes through electrophoretic adsorption. The electrochemical and immersion corrosion tests were conducted under simulated normal conditions using a PBS solution (pH 7) and under inflammatory conditions, achieved by introducing H_2O_2 and HCl (pH 5.2) into the PBS solution.

RESULTS AND DISCUSSION: The experimental results showed that the inclusion of $KMnO_4$ into electrolyte led to a reduction in voltages, while Mn_3O_4 resulted in an elevation in process voltages, directly impacting the structural characteristics of the coatings. Importantly, incorporating these additives decreases surface porosity and increases PEO coating thickness. Electrochemical and immersion corrosion tests, conducted under both simulated normal and inflammatory conditions, underscored the vulnerability of uncoated Mg-Zn-Ca alloy to corrosion, particularly in inflammatory settings (with corrosion rates increasing from approximately 2 to 16 $mm\cdot y^{-1}$). Notably, the composite PEO coatings, incorporating Mn3O4 nanoparticles, displayed superior corrosion performance. This superiority manifested as a significant decrease in corrosion current density and an increase in total impedance resistance compared to basic PEO coatings. For instance, potentiodynamic polarization results indicated a substantial reduction in corrosion current density, decreasing from 73.9 $\mu A\cdot cm^{-2}$ for basic PEO coatings to 5.5 $\mu A\cdot cm^{-2}$ for Mn_3O_4-incorporated PEO coatings. The enhanced performance was attributed to the catalytic activity of Mn3O4 in scavenging H_2O_2 in simulated inflammatory conditions, as well as the greater thickness and lower porosity of the composite coatings compared to basic PEO. Collectively, these features hindered the penetration of corrosive agents to the substrate. Moreover, the coatings showed a controlled release of Mn ions into the surrounding environment within a safe concentration range for the human body.

CONCLUSIONS: These findings suggest that PEO coatings incorporating Mn_3O_4 present promising protective solutions for Mg implants, showcasing improved corrosion behavior associated with inflammation.

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