STUDY OF MOLYBDENUM STABLE OXIDE FILM IN SIMULATED BODY FLUID

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Abstract
This study's main goal is to thoroughly compare the mechanical attributes and biocompatibility of the recently created titanium alloy Ti15Mo7Zr15Ta1Si (62% Ti, 15% Mo, 7% Zr, 15% Ta, 1% Si) to that of the pure metal Mo. The samples underwent a series of meticulous preparation procedures, including chip preparation, polishing, grinding, and cutting, to enable a thorough evaluation. These preparation steps were essential for ensuring the samples' consistency and uniformity, which allowed for accurate and reliable analyses of their mechanical and corrosion-related properties. The samples' microstructure and surface morphology were also investigated using metallographic techniques, allowing a thorough examination of any potential flaws, grain boundaries, or phase compositions.
Additionally, electrochemical tests were used to investigate the materials' corrosion resistance and electrochemical characteristics in environments that mimicked physiological conditions. The samples were subjected to a variety of electrochemical analyses, such as polarization curves and impedance spectroscopy, in order for the researchers to fully comprehend the corrosion behavior of the materials and their suitability for biomedical applications.

Introduction

Titanium is a non-toxic element, even in large doses. Several studies have examined what would happen if humans consumed up to 0.8 mg of titanium daily, showing that Ti was eliminated without being absorbed or assimilated. A number of studies have demonstrated that titanium implants do not experience rejection because of its biocompatibility, favorable interactions with the host bone, and excellent corrosion resistance.
Molybdenum is a substance that is frequently used to alloy titanium Since Mo is a stabilizing element, some research in the field has shown that a percentage of about 20% Mo can reduce the modulus of elasticity and result in proper mechanical properties, similar to those of human bone. With regard to Cr, Ni, and Co, it is also a biocompatible element with a low level of toxicity.
The purpose of this experiment is to compare the degree of corrosion of molybdenum with that of the alloy and to observe if it is quite favorable for the medical environment, so the experiment is carried out in a liquid environment, namely in Ringer's solution.[1]

Experimental

Epoxy resin was first added to molds in a 4:1 ratio to prepare the surfaces of the two samples for embedding. In other words, four drops of resin were added for every one drop of catalyst.

The samples were then longitudinally cut at a thickness of 1 to 1.5 mm using a Buehler IsoMet 4000 precision saw (Buehler, Lake Bluff, IL, USA).
The cutting tool was also used to make roughly 0.5 mm thick vertical cuts. Next, grinding and polishing were carried out in two steps using the Struers TegraPol-11 polishing machine (Struers ApS, Ballerup, Denmark): first, using silicon carbide papers with increasing grit sizes between 280 and 1200,
The samples, which contain Molybdenum metal and Ti15Mo7Zr15Ta1Si alloy, were cleaned and leveled to create a suitable surface for the experiment by using a "Struers" polishing machine at a speed of 150 rpm, for 3-6 minutes, with a force of 20N-40N. After using an 800P grit abrasive paper to remove impurities, they were cleaned with water and alcohol.
The samples were then heated "Ultrasons-HD" ultrasonic equipment from J.P. Selecta (JPS, Barcelona, Spain) for ten minutes to remove any last traces of dirt or contaminants. 4 of 23 surfaces were coated with an alpha alumina suspension to give them a mirror-like sheen. For peer review, see Bioengineering 2022, 9, x. The experimental techniques used to prepare samples for metallography were in accordance with ASTM E3-11(2017). The phases and compounds that make up a metallic material, as well as any impurities or potential mechanical flaws, are arranged spatially in metallography.
In an electrochemical cell with three electrodes—the samples served as the working electrodes, the reference electrode was a saturated calomel electrode, and the counter electrode was a platinum electrode—the samples were sequentially added for the electrochemical tests.
The region of each sample was determined before the tests were carried out. The mmol/L values for the Grifols Laboratories' Ringer solution (Barcelona, Spain) were Na+ 129.9, Cl 111.7, C3H5O3 27.2, K+ 5.4, and Ca2+ 1.8. [1]
The Corrosion Potential, Corrosion Rate, and Electrochemical Impedance Spectroscopy procedures were carried out using the BioLogic Essential SP-150 potentiostat from Seyssinet-Pariset in France. The tests were carried out at 25°C in an aerated Ringer solution.
By entering the sample surface area value and the 20-minute test period, the "Linear Polarization" approach used in these experiments was found to be viable. Data were collected every 0.50 seconds during the potential scanning, which revealed a 0.167 mV/s time-variation relationship between 0.025 and 0.025 V against the open circuit potential (OCP) and an intensity that remained at 100% throughout the procedure. These linear polarization curves were presented and the corrosion rate estimates for each sample were obtained using EC-Lab's "Tafel Fit" technique. The surface value and the five-minute measurement period were entered, and the impedance measurement method was selected as "Potential Electrochemical Impedance Spectroscopy". This measurement was carried out seven times for each sample at 300 mV vs. Ecorr in Ringer's solution, with 10 V being the highest and lowest potential values. To illustrate these data, equivalent circuits and Bode and Nyquist diagrams were used.[3]
The Future Tech FM-810 hardness tester (Kawasaki, Japan) was used to take 10 measurements for each sample's applied load, in this case 1, 5, and 10 gf, in accordance with ISO 14577-1:2015 [32]. The mark may contain fragments from various phases as the stress increases, providing an approximation of the material's overall hardness. When relatively light weights are positioned, it is possible that the mark will only be discovered in one phase, allowing one to gauge the difficulty of that phase. The Vickers microhardness values were then computed automatically by the iVicky software (v2.0, Sinowon, Dongguan, China) using the observed diagonal lengths. The number of indents made were plotted against the scan length.[2]

Results and discussion

With reference to the corrosion potential depicted in Figure 1, it is clear that molybdenum and Ti15Mo7Zr15Ta1Si behave differently. A stable corrosion potential over time indicates that Ti15Mo7Zr15Ta1Si has a significant tendency to passivate, according to the data. By strengthening the material's resistance to corrosion, this passivation phenomenon which is typified by the creation of a protective oxide layer improves its longevity and performance in harsh environments.

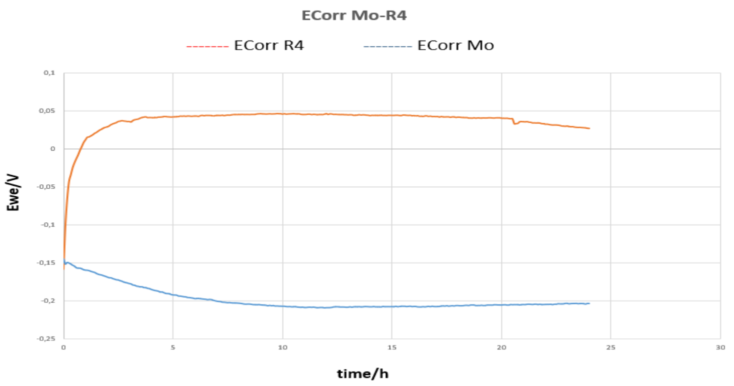

Figure 1. Corrosion Potential

On the other hand, the graph shows that molybdenum corrodes gradually, indicating that it is susceptible to the corrosive effects of the surrounding medium. When using molybdenum in applications where exposure to corrosive agents is anticipated, this gradual corrosion tendency highlights the need for careful consideration. It also highlights the significance of implementing appropriate protective measures or investigating alternative materials with higher corrosion resistance for such environments.

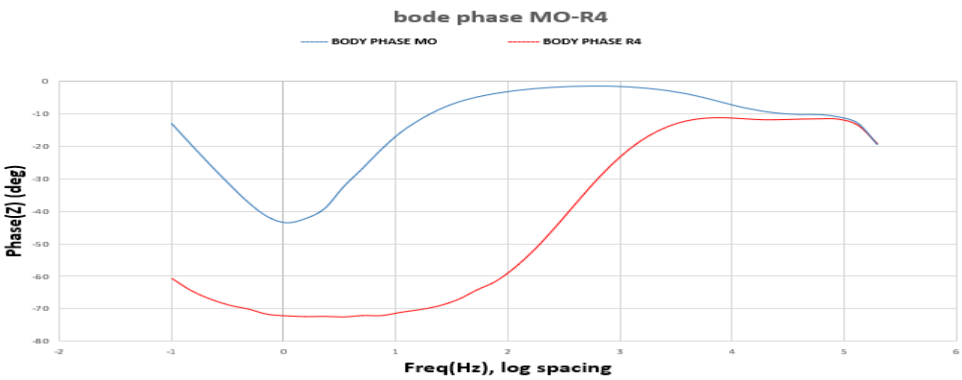

Figure 2. Bode-Phase in Ringer solution

When analyzing the Bode spectra (Figure 2), we can see that Ti15Mo7Zr15Ta1Si has a large zone with a high phase angle (almost -80 deg.), indicating that it has high corrosion resistance properties, while Mo exhibits a narrow, non-point dense pit that may be related to a weak passivating effect that cannot adequately protect the material.

According to the Bode-IZI spectra, which confirmed what had been stated previously in relation to the Bode-phase graph (Figure 2), Ti15Mo7Zr15Ta1Si exhibits high impedance levels, which are indicative of strong corrosion resistance. On the other hand, Molybdenum, characterized by its remarkably lower impedance level, significantly enhances its resistance to corrosion. This property positions it as an invaluable asset in environments where the prevalence of corrosive agents poses a persistent threat to the structural integrity of materials.

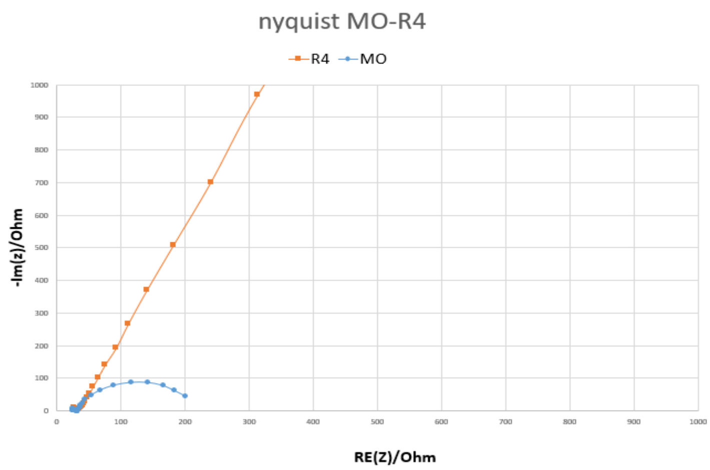

Figure 3. Nyquist spectra in Ringer solution

Finally, it is evident from the data that the Ti15Mo7Zr15Ta1Si alloy, characterized by its remarkable stability, displays a propensity for passivation, a process in which it forms a protective oxide shield. This oxide shield acts as a formidable barrier against corrosion, further enhancing its resistance to the degrading effects of corrosive agents. In contrast, Molybdenum exhibits a different behavior, notably manifesting pitting corrosion phenomena when subjected to potential values of approximately 0.1 V versus the standard saturated calomel electrode (SCE). This observation underscores the vulnerability of Molybdenum to localized corrosion, emphasizing the importance of considering these materials' distinct corrosion characteristics when selecting them for specific applications.

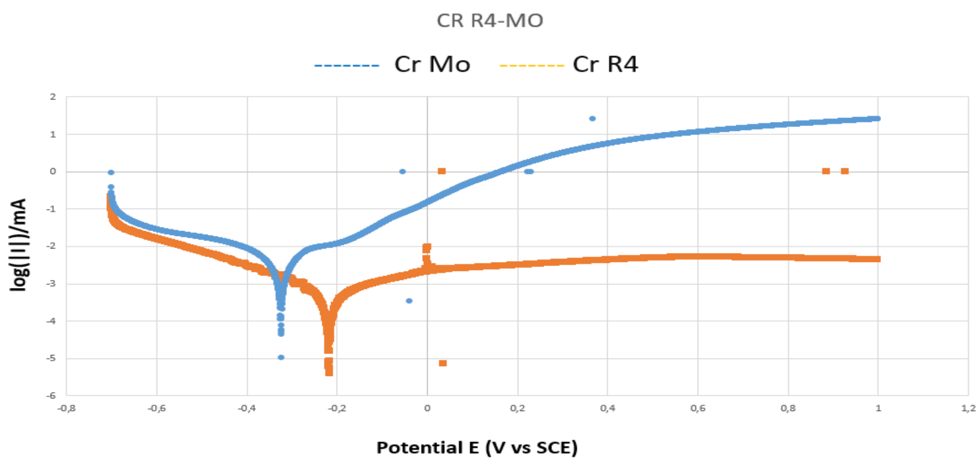

Figure 4. Corrosion Rate

Linear polarization curves in Ringer solution

Conclusion

While molybdenum is typically known for its resistance to corrosion in specific environments, its behavior can change when complex solutions like Ringer's solution are present. This environment in particular, which is frequently used to simulate physiological conditions in biological experiments, contains a variety of ions and substances that may cause specific reactions with molybdenum, resulting in gradual corrosion over time. Due to its exceptional qualities of strong corrosion resistance, remarkable stability, and innate passivating abilities, the Ti15Mo7Zr15Ta1Si alloy stands out significantly. These characteristics make it a very strong candidate for a wide range of biological applications. Its superior corrosion resistance highlights its potential for use in challenging biological and biomedical environments where corrosion can degrade the performance and longevity of materials. This corrosion resistance surpasses that of the commonly used materials. It is ideally suited for implantable medical devices, prosthetics, and other biomedical tools due to its resistance to the physiological conditions found inside the human body and impressive mechanical strength.

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References

[1] Jiménez-Marcos, C., Rosca, J. C. M., Bălţatu, M. S., & Vizureanu, P. (2022). Experimental research on new developed titanium alloys for biomedical applications. Bioengineering, 9(11), 686. https://doi.org/10.3390/bioengineering9110686
[2] Jiménez-Marcos, C., Rosca, J. C. M., Bălţatu, M. S., & Vizureanu, P. (2023). Effect of SI contents on the properties of TI15MO7ZRXSI alloys. Materials, 16(14), 4906. https://doi.org/10.3390/ma16144906
[3] Jiménez-Marcos, C., Rosca, J. C. M., Bălţatu, M. S., & Vizureanu, P. (2023b). Evaluation of new titanium alloys as potential materials for medical devices. Microscopy and Microanalysis, 29(Supplement_1), 196-201. https://doi.org/10.1093/micmic/ozad067.088