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Nanocoatings Prepared by MAPLE Deposition Based on Chitosan (Ch), Bioactive Glass (BG), Titanium Dioxide (TiO_2) and Zinc Oxide Nanoparticles (ZnO)

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Abstract

- The purpose is to obtain new multifunctional formulations based on native titanium oxide (TiO_2), chitosan (Ch), bioglass (BG) and zinc oxide (ZnO) by Matrix Assisted Pulsed Laser Evaporation (**MAPLE**), for biomedical applications.
- In this study, the deposition is carried out on a titanium alloy substrate (73Ti-20Zr-5Ta-2Ag).
- To prepare the suspensions for MAPLE deposition, several samples containing native TiO_2 with Ch, BG and ZnO were produced in various mass ratios which were subsequently characterized.
- The surface morphologies of the 73Ti-20Zr-5Ta-2Ag samples coated and uncoated with native TiO_2 and Ch + BG + ZnO films deposited from mixtures solution were investigated by a scanning electron microscope (**SEM**) equipped with an **EDX** detector.
- The **FTIR** method was used to confirm the qualitative detection of functional groups specific to the native TiO_2 with Ch + BG + ZnO coating.
- The studies of the coatings were also evaluated by **AFM** and by **wettability** determinations.
- The surface roughness is correlated with SEM morphology, proving that the coatings containing larger particles lead to surfaces with higher roughness.
- All the investigations show a good response of the coatings for further biocompatibility applications in medicine.

Acknowledgement

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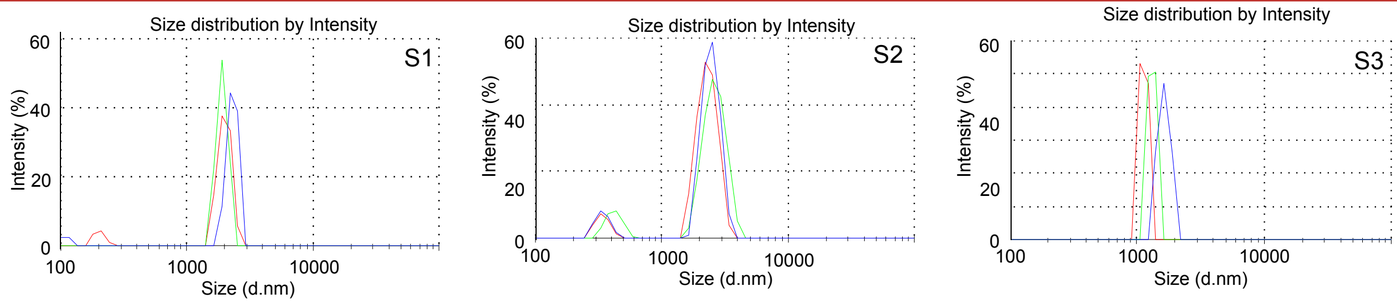
Suspension Particle Size

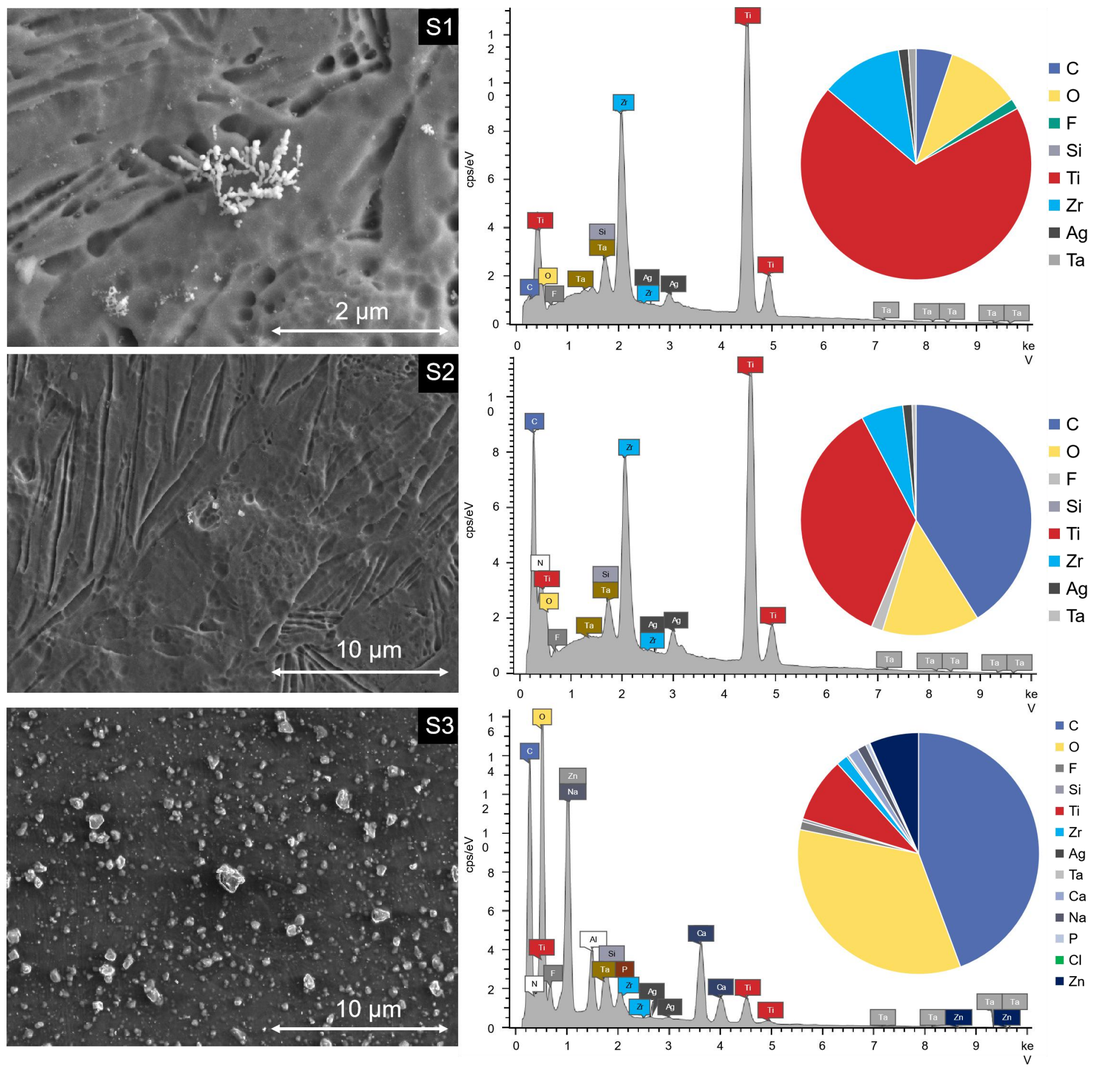


Average particle size	
Sample	D_{50} Z-ave [nm]
S1	1,948 ± 176
S2	2,415 ± 115
S3	1,593 ± 7.07

The average size of the particles is in the range between 1.2 and 2.5 nm.

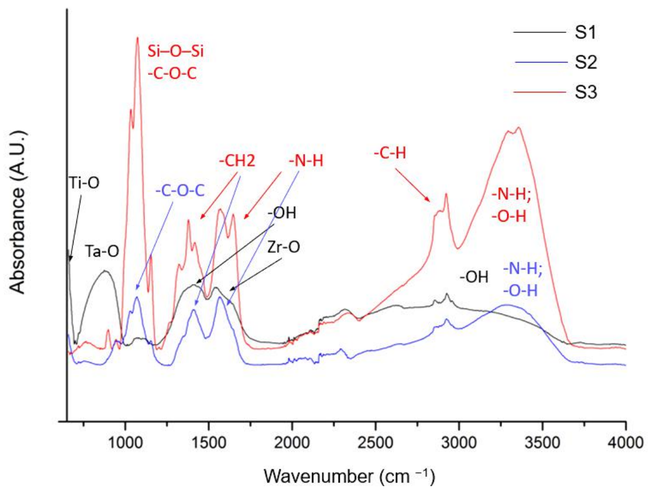
- The sedimentation rate of a suspension depends on the size of the particles, the shape, density as well as on the viscosity of the fluid in which they are suspended. Smaller particle sizes lead to a longer sedimentation time. The high stability of S3 was probably given by the higher polymer to ceramic ratio, which prevented the agglomeration of the suspended particles.

Surface Characterization



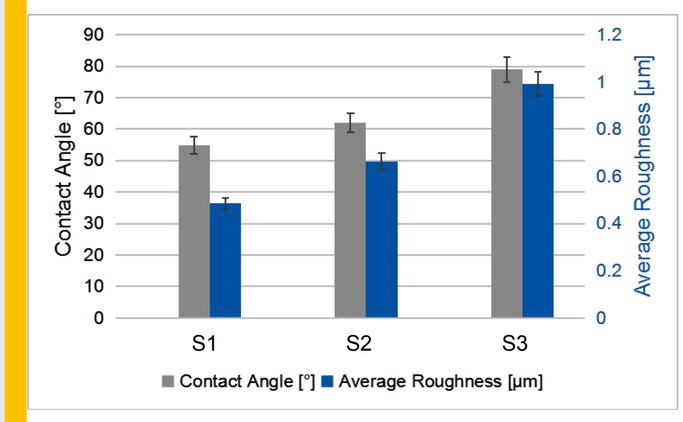
- For S1, a native titanium oxide appear because of the large amount of Ti in the alloy.
- Some Ag particles are present due to the alloy surface composition.
- For S2, the surface is covered with a thin chitosan film deposited above the TiO_2 film.
- On the surface of sample S3 the ceramic particles are well dispersed in the polymeric matrix, with sizes between 0.1 and 1.5 µm.
- Energy Dispersive X-ray Spectroscopy (**EDX**) was used to determine the composition of the surfaces of the samples.
- The EDX spectra and relative atomic weight composition for three representative samples are presented.
- The surface of sample S1 is mainly composed of metallic oxides produced natively, after the etching process.
- Sample S2 shows the increase of carbon percentage from the coating with the chitosan solution.
- On sample S3 all the components from the mixture containing TiO_2, chitosan, bioglass and ZnO are shown to be present on the surface.

FT-IR Characterization



- Characteristic IR absorption peaks of functional groups could be identified and attributed for each component.
- ZnO: Zn-oxygen stretching at 625 cm^{-1}
- Water: O-H stretching at 3700–3184 cm^{-1}.
- Chitosan: C-O-C stretching at 1001 cm^{-1}, C-O stretching at 1066 cm^{-1}, CH_2 bending at 1423 cm^{-1}, N-H bending at 1645 cm^{-1}, C-H stretching at 2877 cm^{-1} and N-H and O-H stretching at 3291–3361 cm^{-1}.
- Bioglass: Si-O vibration at 800 cm^{-1}, Si-O-Si vibration at 1001 cm^{-1}.
- For the etched uncovered Ti-Zr-Ta-Ag alloy, the following peaks were attributed: Ti-O stretching at 690 cm^{-1}, Ta-O stretching at 750 cm^{-1} and Zr-O stretching at 1500 cm^{-1}.

Contact Angle and Surface Roughness (AFM) Measurements



- The increase in the contact angle in the case of the chitosan coating can be attributed to the molecular structure of chitosan. Probably, the absence of groups capable of hydrogen bonds on the surface of the chitosan film can explain the often-observed hydrophobic nature of the chitosan films. The addition of the ceramic mixture leads to an increase in the contact angle, as can be seen from the experimental determinations.
- The surface roughness can be correlated with the SEM morphology, noting that the coatings containing larger particles lead to obtaining surfaces with a higher roughness. However, in this case, the contact angle values are more dependent on the chemistry of the samples than on the surface morphology.