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Effects of different micro-arc oxidation discharge parameters and $AgNO_3$ addition amount on the bioactivity of silver-containing HA coating on titanium substrate

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Abstract

- Hydroxyapatite (HA) possesses excellent bioactivity and biocompatibility. However, its antibacterial ability is poor. Silver (Ag) is widely recognized as the best antibacterial agent, but excessive amounts can also result in cytotoxicity.
- This study employs micro-arc oxidation (MAO) on the surface of Ti substrates to prepare HA coatings containing Ag. Various discharge parameters are utilized, and different concentrations of $AgNO_3$ are added to the electrolyte. The surface morphology, compound composition, and biological activity of each specimen are observed and analyzed.
- The research results show that the Ag element (0.11~0.66 at%) was analyzed in all samples added with $AgNO_3$. The coatings containing Ti, Anatase, Rutile, HA, and DCPD for all samples.
- The coating increased their hydrophilicity and resulted in superior bioactivity (SBF immersion). This means that the presence of silver in the coating of the specimen does not affect bioactivity.

Experimental method

MAO parameters

Variable parameters		Constant parameters		
Applied voltage (V)	$AgNO_3$ (mol/L)	Electrolytes (mol/L)	Duration Time (min)	Applied current (A)
300 400	0 0.001 0.002	0.2 mol/L $(CH_3COO)_2Ca·H2O$ 0.1 mol/L $NaH_2PO_4·2H_2O$	5	0.6

Results and discussion

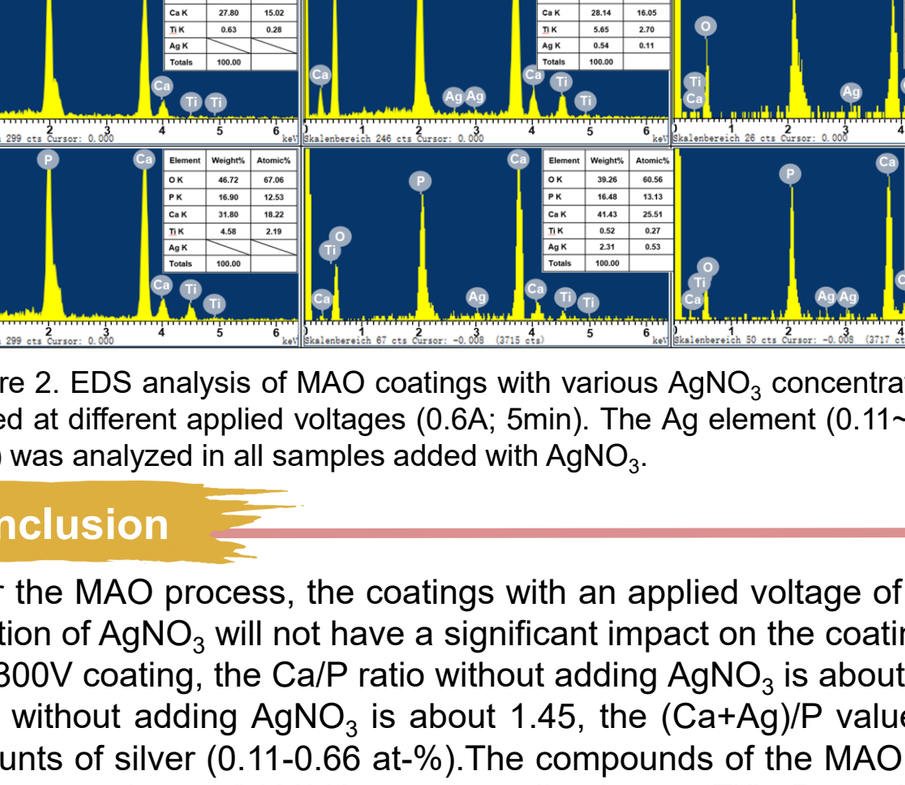

Figure 1. SEM surface morphology of MAO coatings with various $AgNO_3$ concentrations added under different applied voltages (0.6A; 5min). At a discharge voltage of 300V, the coating structure appears a plate-like structure and a small amount of flower-like structure. However, at a discharge voltage of 400V, showing a flower-like structure and a small number of micropores.

Figure 2. EDS analysis of MAO coatings with various $AgNO_3$ concentrations added at different applied voltages (0.6A; 5min). The Ag element (0.11~0.66 at%) was analyzed in all samples added with $AgNO_3$.

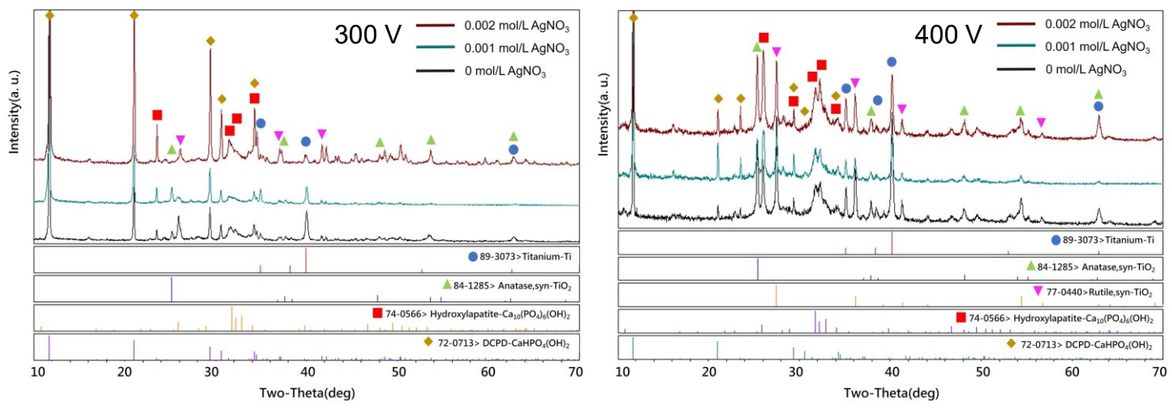

Figure 3. XRD patterns of MAO coatings prepared with different $AgNO_3$ contents added at an applied voltage of 300V and 400 V (0.6A; 5min). The coatings containing Ti, Anatase, Rutile, HA, and DCPD for all samples.

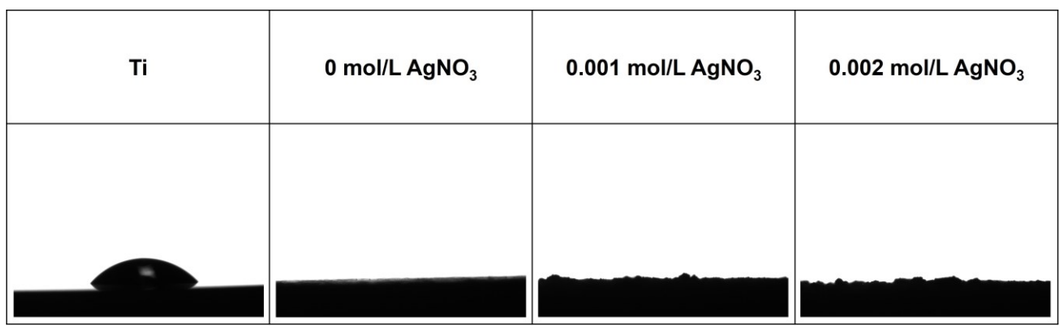

Figure 4. Analysis of contact angle of MAO coating and Ti substrate with different $AgNO_3$ concentrations (400V; 0.6A; 5min). The contact angle of the Ti-based substrate exhibits a certain degree of hydrophilicity (47°). However, all coatings processed by MAO exhibit a contact angle of 0°, demonstrating superhydrophilicity.

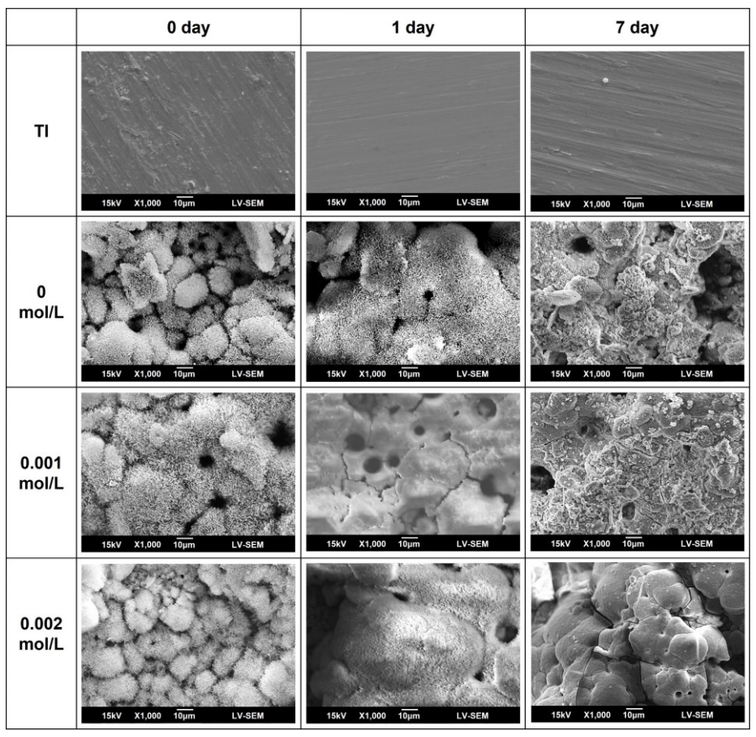

Figure 5. SEM micrographs of the growth of apatite after MAO coatings with different $AgNO_3$ concentrations were soaked in SBF for 0, 1, and 7 days (400V; 0.6A; 5min). After 7 days, the surfaces of all coating samples with $AgNO_3$ added were completely covered with apatites because the release of Ag^+ ions may cause the simultaneous adsorption of Ca^{2+} and PO_4^{3-}, driving the accelerated nucleation of apatite.

Conclusion

- After the MAO process, the coatings with an applied voltage of 300V all showed a plate-like structure; the 400V coatings had a flower-like structure. The addition of $AgNO_3$ will not have a significant impact on the coating structure.
- For 300V coating, the Ca/P ratio without adding $AgNO_3$ is about 1.16, and the (Ca+Ag)/P value with $AgNO_3$ is about 1.19~1.39; for 400V coating, the Ca/P ratio without adding $AgNO_3$ is about 1.45, the (Ca+Ag)/P value when adding $AgNO_3$ is about 1.77-1.98. Coatings with added $AgNO_3$ will contain trace amounts of silver (0.11-0.66 at-%).The compounds of the MAO coating consist mainly of Ti, anatase (TiO_2-A), HA, and DCPD, while the specimen with a discharge voltage of 400V has more rutile phases (TiO_2-R), and its DCPD is significantly lower than 300V.
- MAO coatings are all super-hydrophilic (contact angle 0°) due to the presence of HA and DCPD phases. In the SBF test, after 1 day of immersion, apatite nucleation occurred in all MAO coatings; after 7 days, the surface of the coating added with $AgNO_3$ was roughly covered with apatite.

Acknowledgments

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