

Kinetics of Ag⁺ ion release from TiCaPCON-Ag films: Influence of Ag content and surface roughness

I.V. Sukhorukova*, A.N. Sheveyko, Ph.V. Kiryukhantsev-Korneev, and D.V. Shtansky

National University of Science and Technology (MISiS), Moscow, 119049 Russia

TiCaPCON-Ag films with 1.0 and 2.5 at % Ag were deposited by magnetron sputtering onto Ti substrates with different surface roughness, i.e. (i) polished Ti with average surface roughness $R_a = 20$ nm and (ii) pulsed electrospark treated Ti with $R_a = 8$ μ m. Doping with Ag was found to result in the formation of Ag nanoparticles, 5–10 nm in size, located on the film surface. The kinetics of Ag⁺ ion release from the films into physiological solution was studied by inductively coupled plasma mass spectrometry. It has been demonstrated that the process of Ag⁺ ion leaching out of the surface can be well controlled by varying the substrate surface roughness and the Ag content of the films.

Keywords: magnetron sputtering, TiCaPCON-Ag films, structure, surface roughness, electrochemical study, Ag⁺ ion release

1. Introduction

Implant-related infections remain a serious problem in modern orthopedic and dental surgery. Bacteria and fungi can colonize the surface of an implant forming an adherent biofilm that is difficult to remove by means of traditional antibiotic therapy [1]. One of the effective ways to resolve the problem is by deposition of antibacterial coatings that would minimize the risk of microbial contamination but retain the bioactivity and biocompatibility of the implant surface [2].

To date, Ag is known as one of the most popular dopants to bulk materials and coatings to provide antimicrobial protection against different bacteria. The bactericidal effect is achieved due to transition of Ag⁺ ions into biological environment and their adsorption to bacteria surface, which results in the damage of cell membranes and change in enzyme functions [3].

In the design of antibacterial coatings, it has to be kept in mind that the concentration of an antibacterial agent must be sufficient for suppression of bacteria growth but at the same time be minimal in order to avoid cytotoxicity. The bactericidal effect of Ag-doped materials is known to depend on the amount of Ag⁺ ions that could be released from the surface of a given material [4]. The minimal Ag⁺ con-

centration ensuring bactericidal effect was shown to be 0.1 ppb (10^{-8} %) whereas cytotoxicity becomes clearly pronounced at 10 ppm (10^{-3} %) [3–5]. As a rule, there is no direct relationship between the rate of Ag⁺ ion release into solution and the Ag content of a material. For instance, TiO₂ coatings containing 1.0 at % [6] and 1.63 at % Ag [7] were reported to release strongly different amounts of Ag⁺ ions into solution: 55 and 0.16 ppb, respectively. At the same time, in the case of Ag-doped hydroxyapatite (HA) coatings with 3% and 5% Ag, the maximal Ag⁺ concentration reached in 7 days of testing was 0.2 ppm for both samples [8, 9]. It should also be noted that the kinetics of Ag⁺ ions outflow into solution depends on many factors such as Ag content, its physicochemical state, and specific surface roughness of material. In particular, Ag nanoparticles *per se* can also exhibit their own antibacterial activity [10].

In this work, we explored the influence of Ag content and surface roughness on the kinetics of Ag⁺ ion release from TiCaPCON-Ag films into physiological solution.

2. Materials and methods

In our experiments, we used Ti substrates (Grade 4, ASTM F 67-00) with different average surface roughness R_a : (i) polished Ti with $R_a = 20$ nm and (ii) pulsed electrospark treated Ti with $R_a = 8$ μ m. Pulsed electrospark treatment (PET) was carried out in an Allier-303 unit (pulse duration 80 μ s, pulse repetition frequency 800 Hz, current amplitude 150 A).

* Corresponding author

Irina V. Sukhorukova, e-mail: irina_bttn@mail.ru

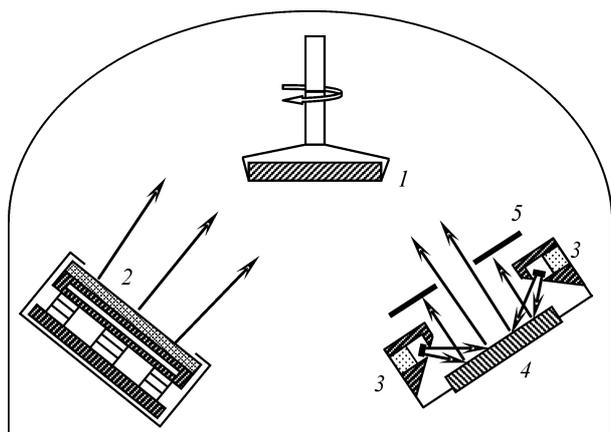


Fig. 1. A schematic of magnetron sputtering: sample holder (1); TiC–Ca₃(PO₄)₂ target (2); ion source (3); Ag target (4); and calibrated aperture (5).

TiCaPCON-Ag films were deposited onto Ti substrates by magnetron sputtering as shown in Fig. 1. The TiC–10%Ca₃(PO₄)₂ target 2 was fabricated by self-propagating high-temperature synthesis (SHS) as described elsewhere [11]. Magnetron current was kept constant at 2 A. Ag dopant was introduced by using additional ion source 3 with calibrated aperture 5. Ion source current was maintained at 50 mA. The calibrated aperture was used to restrict the Ag flow and to reduce the Ag content in the films to a few atomic percent. As a result, Ag contents of 1.0 and 2.5 at % were obtained at applied voltages of 1.5 and 2.0 kV, respectively.

Electrochemical studies were performed in 0.9% NaCl solution (normal saline) at $37 \pm 0.1^\circ\text{C}$ by using a Voltalab PST050 potentiostat (Radiometer Analytical). Temperature-controlled electrochemical cell had an Ag/AgCl reference electrode and a Pt counter electrode. The Ti disks used in the experiments were 15 mm in diameter and 3 mm thick

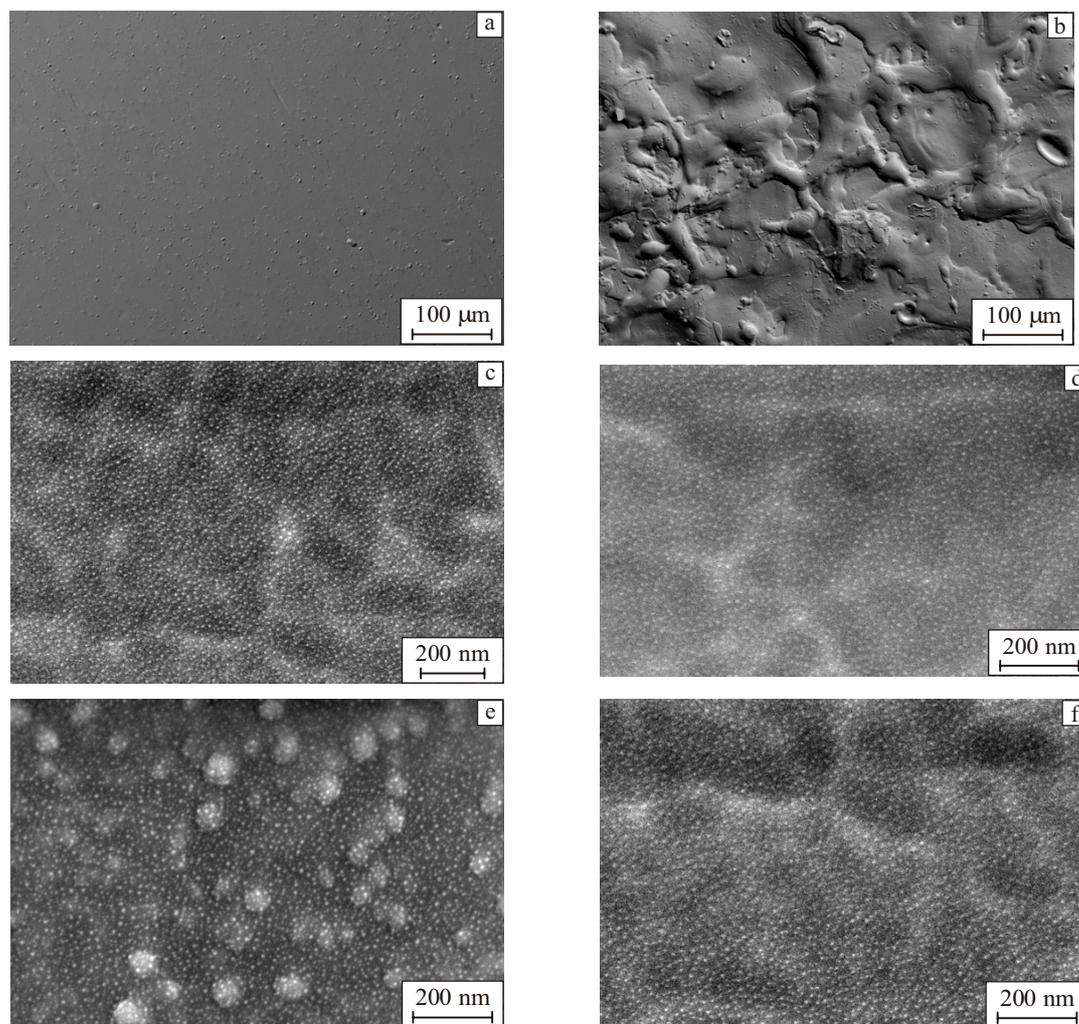


Fig. 2. SEM images of the surface of TiCaPCON-Ag films with (a, b, c, d) 1.0 and (e, f) 2.5 at % Ag deposited onto (a, c, e) polished and (b, d, f) PET-modified Ti substrates.

with a deposited TiCaPCON-Ag film, the other disk surfaces being coated with the Ag-free TiCaPCON film. Initially, free corrosion potential (FCP) was measured as a function of time for 30 min. A steady FCP was then used as a reference in subsequent potentiometric measurements. All potentials were recalculated with respect to the standard hydrogen electrode. Potentiodynamic polarization measurements were performed in the range between -0.1 and $+2.5$ V with respect to the open-circuit potential at a scan rate of 1 mV/s.

The rates of Ag^+ ion release into normal saline were determined by inductively coupled plasma mass spectrometry (ICP-MS) (X-Series II apparatus). Ti samples (15×15 mm in size) with TiCaPCON-Ag films were immersed in 40 ml of 0.9% NaCl solution at room temperature. Then 1.5 -ml probes were sampled at time points of 1 , 3 , 5 , and 7 days and analyzed for Ag.

The Ag depth profiles were determined by glow discharge optical emission spectroscopy (GDOES) using a Profiler 2 spectrometer (Horiba Jobin Yvon). The structure and elemental composition of the films were characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) using a JSM-7600F microscope (JEOL). The surface topography was studied by atomic force microscopy (AFM) using an NTEGRA Spectra NT-MDT apparatus, while average surface roughness R_a was detected with a Veeco Wyko NT1100 optical profilometer.

3. Results and discussion

Our previous structural studies have shown that the Ag-free TiCaPCON films have a nanocomposite structure in which NaCl-type cubic $\text{Ti}(\text{C}, \text{N})$ crystallites (<25 nm in size) are embedded into an amorphous matrix formed by Ca, P, and O elements [12].

Figure 2 shows the SEM images of Ag-doped TiCaPCON films containing 1.0% and 2.5% Ag deposited onto the smooth and rough Ti surfaces. In Fig. 2a, $R_a = 20$ nm, whereas after PET R_a -attained a value of $8 \mu\text{m}$, i.e. more than two orders of magnitude (Fig. 2b). Note that PET resulted in the formation of numerous erosion holes on the substrate surface. Subsequent deposition of TiCaPCON-Ag films with a thickness of several micrometers does not change the initial surface topography. Our analysis of the surface roughness revealed that the overall specific surface increased by a factor of 2.1 . Irrespective of Ag content and surface roughness, the surface of deposited films is seen to exhibit the presence of the Ag nanoparticles 5 – 10 nm in size (Figs. 2c–2f). The distance between the Ag nanoparticles was found to depend on the surface temperature during deposition process while their size—on the Ag content of the deposition flux [13].

Figure 3 presents the AFM images of TiCaPCON-Ag films deposited onto a polished Ti surface. The surface topography of small areas ($5 \times 5 \mu\text{m}$) is defined mainly by the size of Ag nanoparticles. Within these small areas, $R_a = 6$ – 9 nm which is twice smaller than the values (20 nm) determined by optical profilometry over much larger surface areas (0.9×1.2 mm). The size of Ag nanoparticles was observed to increase with increasing Ag content (Fig. 3). The in-depth distribution of Ag as determined by GDOES is presented in Fig. 4. A narrow peak near the surface can be associated with the presence of Ag nanoparticles on the film surface (see Figs. 2c–2f). After a sharp decrease, Ag content is maintained at approximately the same level until reaching the substrate surface. Recently it has been shown that such Ag redistribution is a result of the competition between direct incorporation of Ag atoms into the growing film, surface nucleation of Ag particles, and surface diffusion of Ag atoms [13,14]. Ag atoms are characterized by a

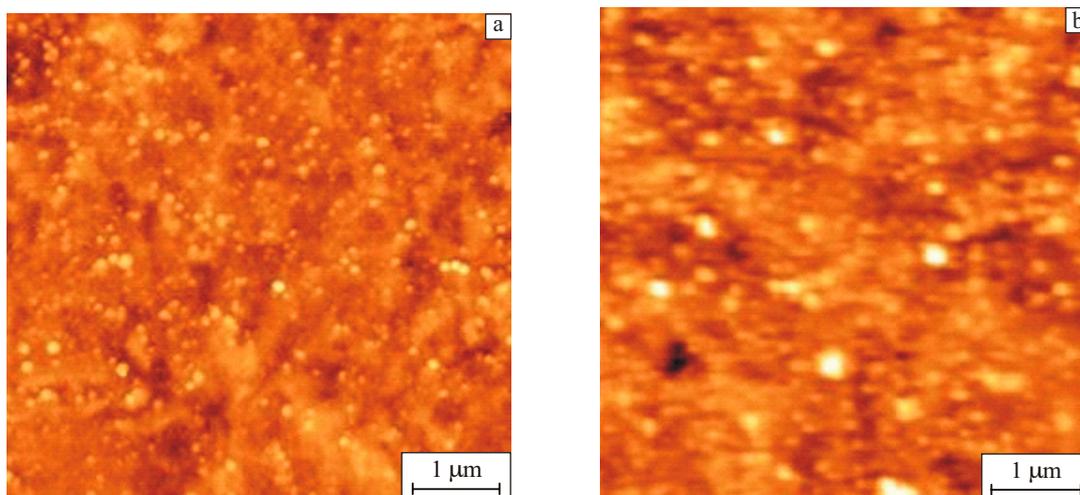


Fig. 3. AFM images of TiCaPCON-Ag films deposited onto a polished Ti surface: 1.0 (a) and 2.5 at % Ag (b).

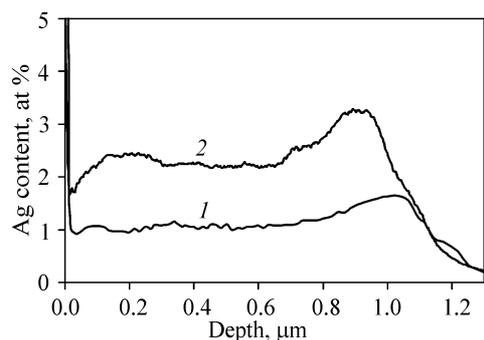


Fig. 4. Ag depth profiles for TiCaPCON-Ag films with 1.0 (1) and 2.5 at % Ag (2), deposited on polished substrates.

high mobility and are immiscible in cubic TiCN phase. With increasing temperature, the mobility of Ag adatoms increased, which led to an increase in effective surface diffusion path. Consequently, the newly deposited Ag adatoms predominantly joined the already existing atoms forming metallic clusters and nanoparticles, whereas the adjacent surface regions become depleted with Ag. The Ag nanoparticles formed on the surface move together with growing film surface. The diffusion coefficient of Ag on the surface of TiCaPCON-Ag films was estimated to be $(0.1 \text{ m}^2/\text{s}) \times \exp(-155 \pm 10 \text{ kJ/mol})$ [15] being in a good agreement with the experimentally determined depth concentration profile of Ag. Some rise in the Ag concentration at a depth of about 1 μm can also be noted. Its existence can hardly be expected to affect the release of Ag^+ ions from the surface. The average Ag content in the films, excluding surface Ag nanoparticles, was 1 and 2.5 at %.

Figure 5 illustrates the kinetics of Ag^+ ion release into physiological solution. For the TiCaPCON-Ag films deposited onto the smooth Ti surface, the amount of released Ag^+ ions only slightly depended on the Ag content (curves 1 and 2). During the first three days, the average rate of Ag^+ ion release was found to be 15 and 20 ppb per day for the films with 1.0 and 2.5 at % Ag, respectively. A difference in Ag concentrations was visible on the fifth day, but then be-

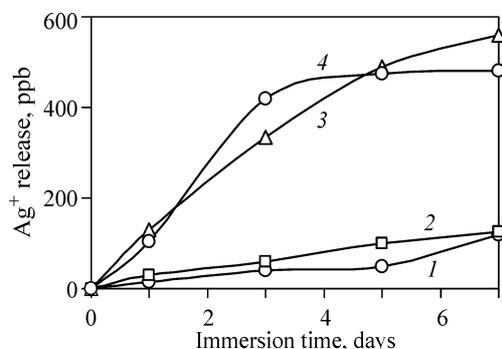


Fig. 5. ICP-MS results for Ag^+ leaching from TiCaPCON-Ag films with 1.0 (1, 3) and 2.5 at % Ag (2, 4) deposited on the surface of polished (1, 2) and PET-modified Ti substrates (3, 4).

came negligible on the seventh day. For the sample with 2.5 at % Ag (curve 2), the release of Ag^+ ions into solution virtually stopped after 5 days.

The influence of the surface roughness on the kinetics of Ag^+ ion release was much stronger than that of the Ag content of the films (Fig. 5, curves 3 and 4). For the films deposited onto a rough Ti surface, the concentration of Ag^+ ions in normal saline attained a level of 100 ppb on the first day, whereas in the case of polished Ti substrates, it took seven days. Note that in the case of PET-modified substrates, the kinetics Ag^+ ion release from the films with 1.0 and 2.5 at % Ag was quite different. In the first three days, both samples demonstrated approximately the same level of Ag^+ ion release, about 100 ppb per day. Starting from the fifth day, however, Ag^+ ion release from the film with a higher Ag content was observed to almost completely stop. Therefore, the films with a higher Ag content exhibited a tendency to slowing down the ion release, irrespective of surface roughness.

In order to find out the reasons for deceleration of Ag^+ ion release from the TiCaPCON-Ag films with 2.5 at % Ag, let us have a glance at their GDOES spectra presented in Fig. 6. It can be seen that the surface of the films becomes Ag-depleted due to dissolution of Ag nanoparticles. So an intense Ag peak in the spectrum of as-deposited film (Fig. 6a) was observed to decrease in its amplitude after 3 days (Fig. 6b) and practically disappear after 7 days (Fig. 6c).

Figure 7 shows the SEM images of the TiCaPCON-Ag film with 2.5 at % Ag deposited onto the smooth and rough Ti surfaces after immersion in NaCl solution for 3 and 7 days. It can be seen that the dissolution of most of the Ag nanoparticles from the smooth surface occurs within seven days (Fig. 7b). Meanwhile, a marked decrease in the amount of Ag nanoparticles on the rough surface was observed after 3 days (Fig. 7c).

Dissolution of Ag nanoparticles and release of Ag^+ ions into normal saline is only one of the chemical reactions that may occur at the film/solution interface. It is well known that the soaking of a bioactive surface in physiological solution may result in a sequence of chemical reactions involving the formation of calcium phosphate and related compounds [16]. Figure 8 presents the IR spectra of TiCaPCON-Ag films with 2.5 at % Ag deposited on the smooth Ti surface taken before (curve 1) and after immersion in NaCl solution for 3 (curve 2) and 7 days (curve 3). The observed increase in the intensity of the bands at 900–1100 and 1300–1500 cm^{-1} is indicative of the presence of $(\text{PO}_4)^{3-}$ groups and CaO on the sample surface. Silver oxide normally exhibits absorption at 530 cm^{-1} . The appearance of this band in spectrum 2 after 3 days clearly demonstrates that, in addition to dissolution, Ag particles also undergo oxidation. The disappearance of this band in the spectrum 3 after 7 days can be explained by a decrease in the amount of Ag particles on the sample surface (Fig. 7b).

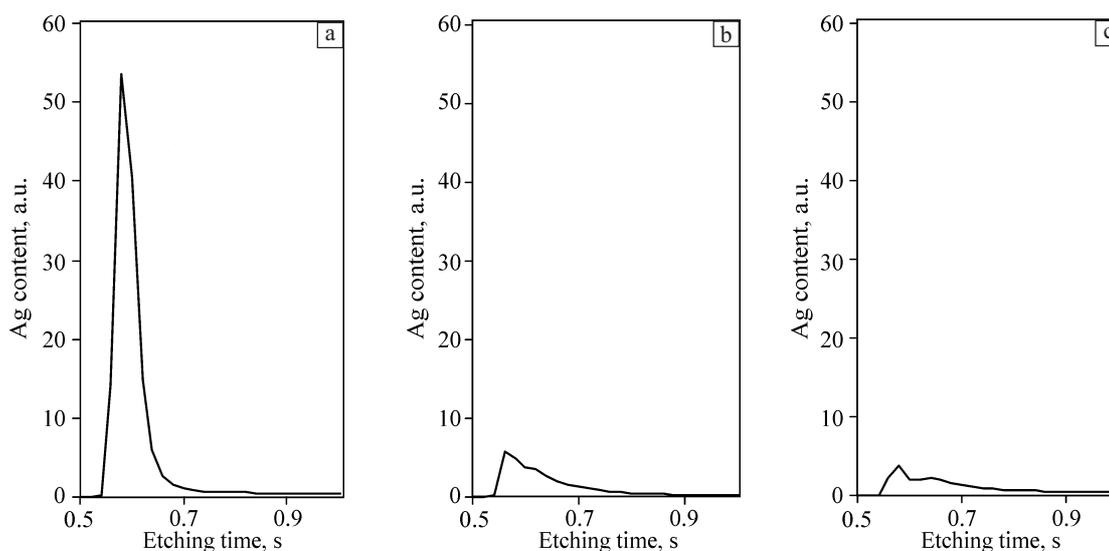


Fig. 6. Ag depth profiles for TiCaPCON-Ag films with 2.5 at % Ag, deposited on the smooth Ti substrates: as-deposited film (a); after 3 (b) and 7 days exposure in NaCl solution (c).

To study the influence of specific surface area on Ag^+ ion release kinetics in normal saline, electrochemical tests were performed and film dissolution currents under polarization conditions were compared. Under a small anodic polarization, it is possible to dissolve all Ag from the sample

surface during a short time period and to compare the results with Ag^+ ion release during sample exposure in physiological solution. For the purpose, we selected the films with 2.5 at % Ag deposited on the surface of both polished and PET-modified Ti substrates.

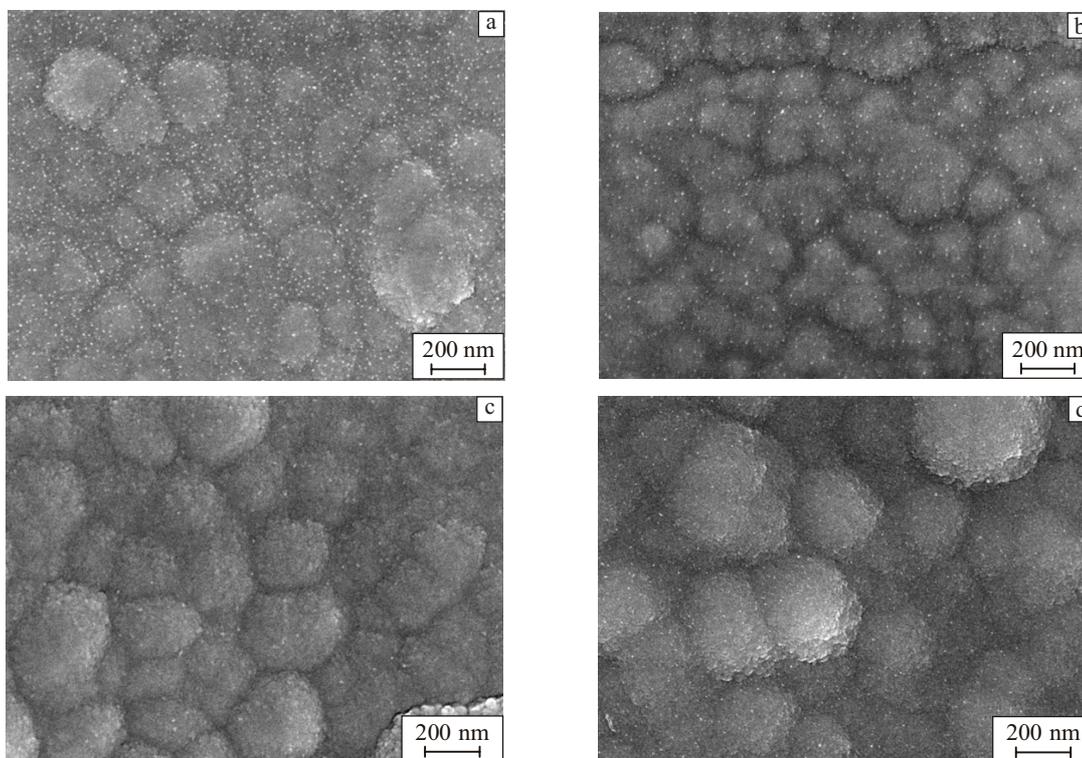


Fig. 7. SEM images of TiCaPCON-Ag films with 2.5 at % Ag deposited on the smooth (a, b) and PET-modified (c, d) Ti surface after exposure in NaCl solution for 3 (a, c) and 7 days (b, d).

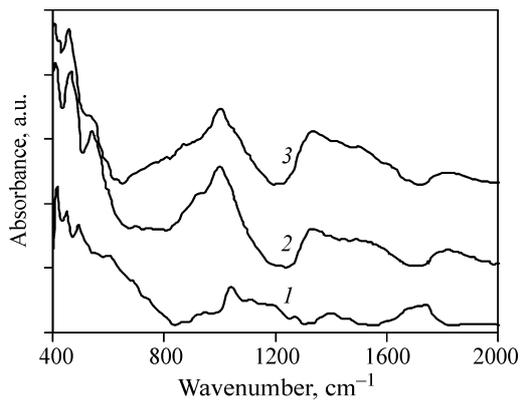


Fig. 8. IR spectra of TiCaPCON-Ag films with 2.5 at % Ag deposited on the smooth Ti surface: as-deposited film (1); after 3 (2) and 7 days exposure in NaCl solution (3).

Figure 9 shows the potentiodynamic polarization curves for the TiCaPCON-Ag films with 2.5 at % Ag. Here we can identify three characteristic regions. For the corrosion potential E around 0.3 V, we observe the characteristic peak of Ag dissolution as described elsewhere [13]. After complete dissolution of Ag nanoparticles, the shape of the curves is defined by the anodic behavior of titanium carbonitride as a main structural constituent of the TiCaPCON film. In the range 0.5–1.5 V, a steady passive behavior of the surface was observed. For $E = 1.5$ –2.0 V the anodic current activation peaks is noted which can be associated with competition between the processes of Ti dissolution and formation of the oxide layer. The current density values of Ag dissolution are seen to be one order of magnitude higher in the case of rough Ti surface (Fig. 9). This agrees with the results presented in Fig. 5. The anodic currents in the range 0.7–1.5 V correspond to dissolution of Ti via the passive oxide layer formed on the surface. Note that these parts of anodic polarization curves correspond to a situation when Ag nanoparticles have already completely dissolved. Within this range, the current density values for the smooth and rough surfaces differ by a factor of about three, which can

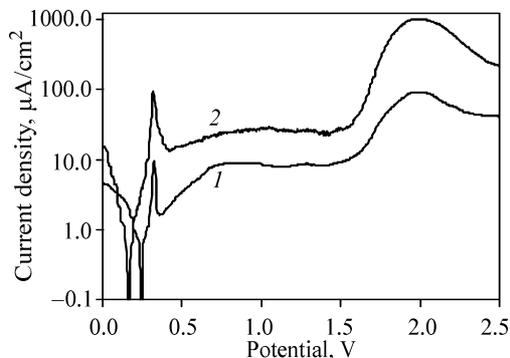


Fig. 9. Anodic potentiodynamic polarization curves for TiCaPCON-Ag films with 2.5 at % Ag deposited on polished (1) and PET-modified Ti surface (2).

be readily explained by a 2.1-fold difference between respective R_a values.

Therefore, our results suggest that the release of Ag^+ ions from TiCaPCON-Ag films into normal saline depends both on the Ag content and on surface topography. The kinetics of Ag^+ ion release is controlled by the dissolution rate of Ag nanoparticles, the latter being markedly higher in the case of rough surfaces. The absolute concentration of Ag^+ ions in physiological solution is affected much stronger by the surface topography than by the film Ag content. A 2.1-fold increase in the surface roughness caused by the preceding PET treatment of the substrate surface lead to a 6–8-fold increase in the amount of Ag^+ ions released during 3 days of soaking in normal saline. Meanwhile, the role of the film Ag content becomes more pronounced at the later stages of dissolution (3–5 days of observation). In particular, Ag^+ release from films with a higher Ag content slows down with time.

4. Conclusions

The kinetics of Ag^+ ion release from TiCaPCON-Ag films into physiological solution was studied as a function of the film Ag content and substrate surface roughness. An increase in Ag^+ ion concentration in normal saline is caused by dissolution of the Ag nanoparticles (5–10 nm in size) formed on the film surface during deposition. An increase in the specific surface area markedly accelerates the release of Ag^+ ions into solution. An increase in the film Ag content results in faster dissolution of Ag nanoparticles at the initial stages but favors earlier exhaustion of the surface.

Acknowledgments

This work was financially supported by the Russian Ministry for Education and Science (Agreement 14.578.21.0086, Identification No. RFMEFI57814X0086).

References

- Duran LW. Preventing medical device related infections. *Med Device Technol.* 2000; 11(16): 14–17.
- Neoh KG, Wang R, Kang ET. *Biomaterials and medical device-associated infections.* Amsterdam: Elsevier; 2015.
- Simonetti N, Simonetti G, Bougnol F, Scalzo M. Electrochemical Ag^+ for preservative use. *Appl Environ Microbiol.* 1992; 58(12): 3834–3836.
- Zhao G, Stevens SE. Multiple parameters for the comprehensive evaluation of the susceptibility of *Escherichia coli* to the silver ion. *Biomaterials.* 1998; 19(1): 27–32.
- Kumar R, Munstedt H. Silver ion release from antimicrobial polyamide/silver composites. *Biomaterials.* 2005; 26: 2081–2088.
- Jamuna-Thevi K, Bakar SA, Ibrahim S, Shahab N, Toff MRM. Quantification of silver ion release, in vitro cytotoxicity, and antibacterial properties of nanostructured Ag doped TiO_2 coatings on stainless steel deposited by RF magnetron sputtering. *Vacuum.* 2011; 86: 235–241.

7. Song D-H, Uhm S-H, Lee S-B, Hanc J-G, Kim K-N. Antimicrobial silver-containing titanium oxide nanocomposite coatings by reactive magnetron sputtering. *Thin Solid Films*. 2011; 519: 7079–7085.
8. Ruan HJ, Fan CY, Zheng XB, Zhang Y, Chen YK. *In vitro* antibacterial and osteogenic properties of plasma sprayed silver-containing hydroxyapatite coating. *Chin Sci Bull*. 2009; 54(23): 4438–4445.
9. Chen Y, Zheng X, Xie Y, Ding C, Ruan H, Fan C. Anti-bacterial and cytotoxic properties of plasma sprayed silver-containing HA coatings. *J Mater Sci: Mater Med*. 2008; 19(12): 3603–3609.
10. Kelly PJ, Li H, Benson PS, Whitehead KA, Verran J, Arnell RD, Iordanova I. Comparison of the tribological and antimicrobial properties of CrN/Ag, ZrN/Ag, TiN/Ag, and TiN/Cu nanocomposite coatings. *Surf Coat Technol*. 2010; 205: 1606–1610.
11. Shtansky DV, Kiryukhantsev-Korneev PhV, Bashkova IA, Sheveiko AN, Levashov EA. Multicomponent nanostructured films for various tribological applications. *Int J Refract Met Hard Mater*. 2010; 28: 32–39.
12. Shtansky DV, Levashov EA, Sukhorukova IV. Multifunctional bioactive nanostructured films, in: Mucalo MR, editor. *Hydroxyapatite (HAP) for Biomedical Applications*. Woodhead Publishing; 2015.
13. Sheveiko AN, Batenina IA, Kiryukhantsev-Korneev FV, Shtanskii DV. Comparative study of the structure and chemical properties of nanocomposite TiCaPCON-Ag coatings. *Protect Met Phys Chem Surf*. 2015; 51(3): 416–426.
14. Sukhorukova IV, Sheveyko AN, Kiryukhantsev-Korneev PhV, Anisimova NYu, Gloushankova NA, Zhitnyak IV, Benesova J, Amler E, Shtansky DV. Two approaches to form antibacterial surface: doping with bactericidal element vs drug loading. *Appl Surf Sci*. 2015; 330: 339–350.
15. Klinger L, Shtansky DV, Levashov EA, Rabkin E. Kinetic model of co-deposition of thin multicomponent films. *Mater Lett*. 2015. <http://dx.doi.org/10.1016/j.matlet.2015.05.013>.
16. Ohtsuki C, Kushitani H, Kokubo T, Kotani S, Yamamuro T. Apatite formation on the surface of Ceravital-type glass-ceramic in the body. *Biomed Mater Res*. 1991; 25: 1363–1370.