

Silver-Doped Layers of Implants Prepared by Pulsed Laser Deposition

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ABSTRACT

Physical and mechanical properties of silver-doped layers of titanium alloy Ti6Al4V and 316L steel prepared by pulsed laser deposition were studied. Metallic silver-doped coatings could be a new way for antibacterial protection in medicine. Thin films of silver and silver-doped materials were synthesized using KrF excimer laser deposition. The material was ablated from two targets, which composed either from titanium alloy with silver segments or from steel with silver segments. The concentration of silver ranged from 1.54 at.% to 4.32 at.% for steel and from 3.04 at.% to 13.05 at.% for titanium alloy. The layers properties such as silver content, structure, and adhesion were measured. Adhesion was studied using scratch test.

Keywords: Thin Layer; Silver; Titanium Alloy; Steel; Pulsed Laser Deposition; Adhesion; Implant

1. Introduction

One of the most serious complications of surgical treatment of fractures is infections. The infectious complications prolong healing and prevent fractures healing deplete the body's immune system. The solution usually requires repeated surgeries and multiplies healing costs and inconvenience for patients. The aim of this work is to find method to create antibacterial materials that will reduce the possibility of an infection or severity of infectious complications in patients after the surgical treatment of fractures. The use of fixation screws for temporary immobilization of broken bones entails considerable risk of infection due to the possibility of the bacteria spread along the outside surface of the fixing screws into the body (see **Figure 1**). Since the silver is known for its excellent antibacterial properties, the use of it as a suitable dopant seems like viable road to take. Coated of implants was given by pulse laser deposition. Silver concentration for various deposition conditions, films structure and adhesion were also studied [1,2].

2. Experimental

Deposition. Silver-doped layers of titanium alloy Ti6Al4V and 316L steel were prepared by PLD using a KrF excimer laser ($\lambda = 248$ nm, $t = 20$ ns, rep. rate of 10

Hz) (see **Figure 2**). The laser beam was focused on a silver target with energy density of 2 Jcm^{-2} , silver with Ti6Al4V or silver with 316L steel targets with energy density of 5 Jcm^{-2} . Material was ablated from one target

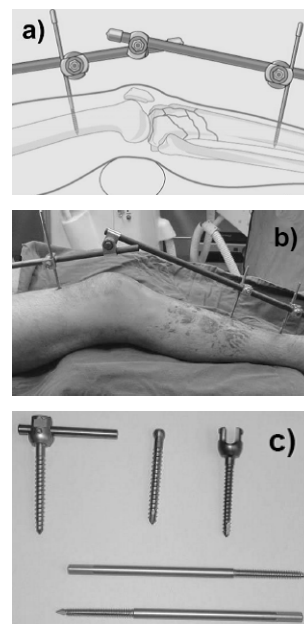


Figure 1. (a) Scheme of application of fixation screws; (b) Photo of application of fixation screws; (c) Fixation screws.

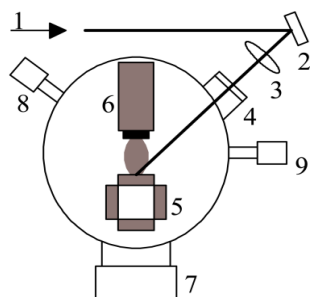


Figure 2. The basic scheme of the experimental apparatus for PLD: (1) laser beam, (2) mirrors, (3) focusing lens, (4) quartz window, (5) target holder, (6) substrate holder, (7) vacuum pump, (8, 9) Pirani and Penning vacuum gauges, respectively.

composed from silver and titanium alloy or steel segments. Substrate (Ti6Al4V, 316L steel or Si (100)) was 35 mm away from target. Substrate was held at room temperature. Films were grown in argon atmosphere of 0.25 Pa. The substrates were cleaned by RF discharge before deposition process.

Thickness and roughness was measured by Alpha-step IQ mechanical profilometer (KLA Co.).

Concentration of silver was determined using WDX measurement (WDX—wavelength dependence X-ray analysis) was analyzed with EDAX Jeol Supersprobe 733.

Structure of layers was determined by XRD in parallel beam geometry and detector scan with stationary sample and glazing angle of incidence (GAOI) were used.

Adhesion. For the adhesion measurements we used macro scratch tester REVETEST (CSM Instruments co.).

3. Results and Discussion

Thickness of PLD created silver layers was 100 nm and 350 nm and thickness of PLD created silver-doped layers was from 94 nm to 398 nm, depending on target, see in **Table 1**.

Roughness of silver-doped 316L steel films was from 12 nm to 29 nm and the roughness of silver-doped titanium alloy Ti6Al4V films was from 5 nm to 28 nm, see in **Table 1**.

Silver concentration - WDX measurement confirmed the increasing concentration of silver with increasing segment of the silver piece on the target - during deposition process. For the layers of 316L steel doped by silver amount of silver is more complicated, see in **Table 1**. of PLD created silver layers was 100 nm and 350 nm and thickness of PLD created silver-doped layers was from 94 nm to 398 nm, depending on target, see in **Table 1**. The concentration of silver ranged from 1.54 at.% to 4.32 at.% for steel and from 3.04 at.% to 13.05 at.% for titanium alloy. It confirmed the increasing concentration of silver with increasing size of silver target during the deposition process. This increase is clear for titanium alloy

Table 1. The deposition condition for fabrication of silver-doped thin films by PLD process, the thickness, roughness and concentration of silver in the layers.

Sample	Substrate	Roughness Ra [nm]	Thickness [nm]	Target (Size)	At. [%] of Ag
Ag-1	Ti6Al4V	-	100	Ag	100
Ag-2	Ti6Al4V	-	350	Ag	100
S-1	316L steel	13	161	316L steel: Ag (40:1)	1.54
S-2	316L steel	29	260	316L steel: Ag (20:1)	4.32
S-3	316L steel	12	94	316L steel: Ag (10:1)	(3.53)
T-1	Ti6Al4V	5	398	Ti6Al4V: Ag (40:1)	3.04
T-2	Ti6Al4V	28	294	Ti6Al4V: Ag (20:1)	5.05
T-3	Ti6Al4V	25	198	Ti6Al4V: Ag (10:1)	13.05

layers. For the layers of 316L steel doped by silver the amount of silver concentration dependence is not monotone and is more complicated, see in **Table 1**.

Crystallinity. In the XRD spectrum of silver-doped 316L steel films were identified peak of intermetallic compounds (compound silver with Fe, Cr, Ni, and Mo). In the XRD spectrum of the titanium alloy doped by silver there are no new peaks, see in **Figures 3(a)** and **(b)**.

Adhesion. For samples Ag-1 and Ag-2 of pure silver layers we used linear progressive scratch with initial load 1 N and the end load 5 N. Loading rate was 4 N/min. Length of the scratches were 8 mm. Two scratches were performed on each sample. The layers were very soft and were penetrated at the start by initial load. For sample Ag-1 there was no delamination observed. For sample Ag-2 we observed delamination for critical force approximately 1.75 N, see in **Figure 4**. Pure silver has low adhesion.

For samples S-1, S-2, S-3, T-1, T-2, and T-3 we used linear progressive scratch with initial load 1 N and the end load 30 N. Loading rate was 15 N/min. Length of the scratches were 5 mm. Two scratches were performed on each sample. Samples were tested for two various roughnesses of substrates, polished and lathed. Both substrates had similar behavior. We did not observe any penetration through layer or delamination. The behavior of the samples was similar to bulk material, see in **Figures 5(a)** and **(b)**.

4. Conclusion

The metallic (titanium alloy Ti6Al4V and 316L steel) layers with various concentration of silver were prepared by PLD. Composition was determined by WDX. The amount of silver in Ti6Al4V layers was from 3.04 to 13.05 at.%. The amount of silver in 316L steel layers was from 1.54 to 4.32 at.%. Minor changes were observed in

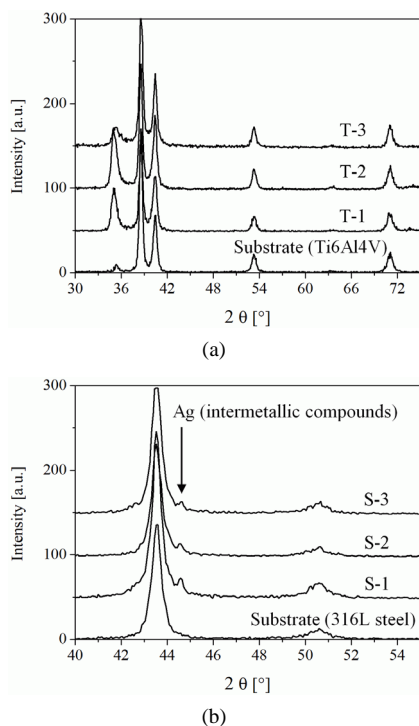


Figure 3. (a) XRD spectra of silver-doped 316L steel layers on 316L steel substrate; (b) XRD spectra of silver-doped titanium alloy Ti6Al4V layers on titanium alloy Ti6Al4V substrate.

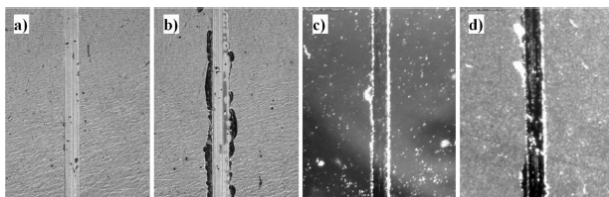


Figure 4. Example of delamination of 350 nm thick silver layer (Ag-2) load 1.4 N (a) and load 1.75 N (b). Comparison of adhesion for 100 nm (Ag-1) (c) and 350 nm (Ag-2) (d) thick silver layers for the force of 4 N.

crystalline structure of the doped steel, which can be assigned to intermetallic compounds with silver. We did not observe new peaks in XRD spectrum of the titanium alloy doped by silver. No silver crystalline phase was found. All layers surfaces were covered with droplets. The adhesion of the silver-doped 316L steel and Ti6Al4V

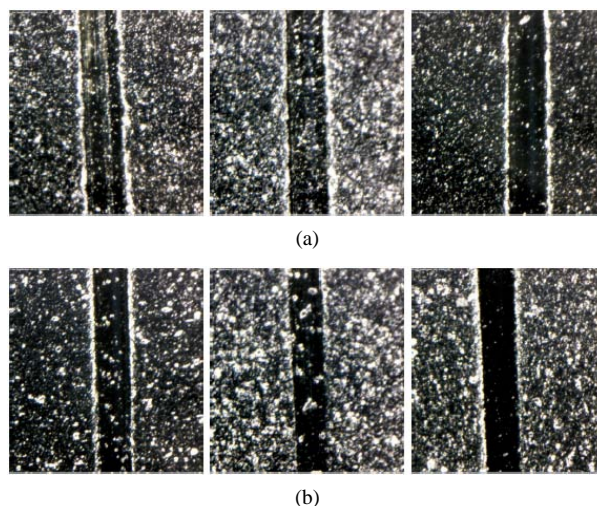


Figure 5. (a) Example of macro scratch on the layers of Ag doped steel 316L. From left sample S-1, S-2 and S-3 (load for all samples 24 N); (b) Example of macro scratch on the layers of Ag doped Ti6Al4V alloy. From left sample T-1, T-2 and T-3 (load for all samples 24 N).

was outstanding. We did not observe any delamination of layers. The transition between the layer and substrate was not observed.

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