Silver nanoparticles formation over Ti-Zr-Nb alloy via polyol synthesis

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Abstract. Ag nanoparticles (AgNPs) were formed over the surface of novel superelastic Ti-Zr-Nb alloy via polyol synthesis at room temperature. Two synthesis media were used for AgNPs formation: ethylene glycol (EG) and polyethylene glycol (PEG-400). AgNPs formation rate in different polyols was evaluated by UV-VIS spectroscopy. Based on the obtained results higher formation rate was ascribed to PEG-400. Morphology of the material’s surface, as well as chemical composition, were analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). It was demonstrated that the usage of PEG-400 as synthesis media facilitates the formation of more monodisperse AgNPs evenly distributed over the alloy’s surface.

1. Introduction
Shape memory alloys (SMA) draw significant attention as the materials for bone tissue replacement [1,2]. These alloys demonstrate superelastic behavior at room temperature (RT) as well as high corrosion resistance which makes them perfect candidates for bone tissue replacement material [3,4]. Recently a novel SMA Ti-18Zr-15Nb with enhanced functional properties was developed [5].

The success of implantation is determined by several factors, the most important of which is the absence of inflammatory processes caused by a bacteria activity at the interface between the bone tissue and the metallic material [6]. For this reason, the development of ways to provide the surface of the implant material with antibacterial properties is an important scientific task.

Silver nanoparticles are well-known for their antibacterial properties. There are many methods of silver coatings and NPs formation over various substrates such as magnetron sputtering [7], electrochemical methods [8], plasma spraying [9], acid- or alkali-heat treatment [10], and so on. In the case of superelastic titanium alloys implemented as a substrate, it is essential to develop specific AgNPs formation methods eliminating the needs of elevated temperatures and even strong reducing agents. Such a feature is explained by the fact that the superelastic properties of Ti alloys depend strongly on their structure and phase composition. For many prospective systems such as Ti-Zr-Nb secondary phases precipitation such as ω-phase takes place at a quite low temperature (300 °C) [11, 12]. Uncontrolled ω-phase formation leads to embrittlement of the material and superelastic properties decrease.

Polyol synthesis is a method of AgNPs formation where the reduction process can be controlled solely by organic compounds – polyols. This method is extensively used for the synthesis of various
transition metals nanoparticles and bimetallic systems [13, 14]. The development of this method enabled many synthesis possibilities to control metallic NPs's structure, morphology, concentration on the surface of the substrate, and their chemical composition [15]. This makes polyol synthesis an attractive technique for the task of AgNPs formation over the surface of superelastic Ti alloys.

Synthesis media and synthesis time have a significant influence on the structure and the properties of the final product. For that reason, in our current work, we investigate the influence of different synthesis media such as ethylene glycol (EG) and low-molecular polyethylene glycol (PEG-400) and synthesis time on the structure of the AgNPs deposited over the surface of superelastic Ti alloy. One of the most prospective alloys of the Ti-Zr-Nb system Ti-18Zr-15Nb was selected as the substrate for the current study.

2. Materials and methods
Small plates (10x5x2 mm) of the superelastic Ti-18Zr-15Nb alloy were used as a substrate for the formation of silver nanoparticles. Plates were subjected to thermomechanical treatment (cold rolling with 25% thickness reduction rate and post-deformational annealing at 550°C for 30 min) enhancing superelastic properties of the material [16]. Surface preparation was carried out by grinding with abrasive paper (up to P2000) and polishing on a polishing fabric using a diamond suspension. Obtained in such manner samples were subjected to sonication in an ultrasonic bath filled with isopropanol alcohol before further manipulations.

For typical synthesis, the glass with a certain amount of the polyol was placed on a magnetic stirrer at 1000 rpm. The substrate was immersed in the media and a freshly prepared AgNO₃ solution was quickly added. The synthesis continued for a required period, after which the substrate was taken out and placed in a glass with distilled water. The glass was placed in an ultrasonic bath for 30 minutes to remove residual polymer and secondary synthesis products from the surface of the alloy. Obtained in such manner samples were dried overnight at ambient air. Table 1 collects the sample description.

| Sample       | Synthesis media | Time, min |
|--------------|-----------------|-----------|
| TiAg_EG_1    | EG              | 1         |
| TiAg_EG_10   | EG              | 10        |
| TiAg_PEG_1   | PEG-400         | 1         |
| TiAg_PEG_10  | PEG-400         | 10        |

XRD analysis was performed on the Dron-3 diffractometer. CuKα radiation with a wavelength of 1.5406 Å was used. The influence of synthesis time on AgNPs formation rate was evaluated by optic spectroscopy using OceanOptics Flame equipment. The surface structure of the obtained samples was analyzed using a scanning electron microscope (SEM) JEOL 5600. The chemical composition of the material was studied by energy dispersive spectroscopy (EDS).

3. Results and discussion
Figure 1 shows the typical XRD pattern of Ti-18Zr-15Nb alloy after AgNPs deposition. It can be seen that the alloy contains only a high-temperature β-phase, which can be determined by four lines (110), (200), (211), (220).
The absence of signals characteristic for ω-phase confirms that the selected synthesis scheme does not lead to changes in the phase composition of the alloy. It should be noted that the signal from AgNPs can not be seen either. It points to the fact that the synthesis time is not high enough for thick Ag layer formation.

UV-VIS spectra of the synthesis media corresponding to different samples are given in figure 2.

It can be seen from figure 2a that in the case of EG and 1 min of the synthesis time no plasmon peak appears in the studied range of wavelength. It indicates that at the given time EG is not efficient enough as a reducing agent hence the formation of a noticeable amount of AgNPs does not take place. On the other hand, at 10 min of synthesis, a pronounced peak is observed at 450 nm (figure 2b). It should be noted that the plasmon peak position shifts to larger values of the wavelength for NPs with larger sizes. It can be concluded that while the AgNPs formation process occurs, the stabilizing effect of the EG is rather weak and NPs growth rate is relatively high. In the case of PEG-400 significant signal can be observed starting from the 1 min of synthesis (figure 2c). What is more interesting is that...
the peak is located at a lower wavelength value (415 nm) which corresponds to smaller sizes of AgNPs. Such a feature should be ascribed to a more pronounced stabilizing effect of PEG-400. At higher synthesis time the peak position shifts to the 435 nm reflecting the AgNPs growth process. Nonetheless, the maximum is still at the lower wavelength as compared to the EG_10 sample. It should be noted that in the case of synthesis media of the PEG-400_10 sample a new signal occurs at approximately 640 nm. It can be suggested that AgNPs of a new morphology are formed as synthesis time rises [17].

Electron images of the surfaces of all obtained samples are shown in figure 3. Silver nanoparticles were formed on the surfaces of all samples as a result of synthesis. It is important to note that there is no contradiction between the results obtained for the TiAg_EG_1 sample by optical spectroscopy and SEM since the former describes synthesis media exclusively. NPs formation process is facilitated significantly on the surface of the substrate. So while there is not a sufficient amount of AgNPs in the whole volume of the synthesis media they can be found on the surface of the alloy immersed into the media.

Figure 3. Electron images of the surface: (a) TiAg_PEG-400_1; (b) TiAg_PEG-400_10; (c) TiAg_EG_1; (d) TiAg_EG_10; (e) EDS analysis TiAg_EG_10.

It can be seen from figure 3a, b that AgNPs are distributed evenly on the surface of TiAg_PEG-400_1 and TiAg_PEG-400_10 samples and their size rarely exceeds 100 nm. In general similar picture is observed for TiAg_EG samples but occasionally agglomerates of larger AgNPs can be found on the surface of the alloy along with the smaller nanoparticles. It can be seen from figure 3c, d that the size of the agglomerate increases as synthesis times rises. The fact that the observed agglomerates consist of AgNPs was further supported by the results of the EDS analysis (figure 3e). It can be suggested that the observed difference in the surface structure of the obtained samples is related to the different stabilizing properties of the media. According to the obtained results, PEG-400 facilitates the formation of more monodisperse AgNPs uniformly distributed over the Ti-18Zr-15Nb alloy as compared to EG.

Figure 4 depicts the results of the EDS analysis conducted for the TiAg_PEG-400_1 sample. Based on SEM studies it was suggested that AgNPs on the surface of the TiAg_PEG-400_1 sample have a core-shell structure. To confirm this suggestion EDS profile was obtained for one of the larger AgNPs (figure 4a). According to the obtained results signal from alloy’s components decreases significantly as the Ag signal increases which confirms that the observed NPs are silver. What is more important is that the intensity of the C signal increases noticeably as well. Comparison of electron image and concentration profiles for Ag and C allows us to suggest that there is a shell around the Ag NP which consists of an intermediate compound containing both polymer and silver. It can be suggested that the observed feature of AgNPs structure in the TiAg_PEG-400_1 sample is due to the specific interaction of polyol macromolecules and AgNO₃ at the early stages of the synthesis.
4. Conclusion
AgNPs were successfully deposited on the surface of Ti-18Zr-15Nb alloy via polyol synthesis. Two synthesis media were used for the deposition process: EG and PEG-400. It was demonstrated that PEG-400 allows us to obtain more monodisperse and evenly distributed AgNPs on the surface of the alloy which makes it more preferable synthesis media as compared to EG. Results of SEM and EDS studies elucidated that at early synthesis stages AgNPs deposited on the surface of Ti-18Zr-15Nb alloy in PEG-400 have a core-shell structure. It was suggested that the shell consists of an intermediate polymeric-Ag compound. Obtained results demonstrate that polyol synthesis can be potentially used for providing the surface of novel superelastic Ti alloys with antibacterial properties.

5. Acknowledgment
The present work has been carried out with the financial support of the Russian Science Foundation (Project №. 19-79-10270).

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