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Effect of Thermal Annealing Temperature on Tri-Layered AgO/AgTaO/TaO Nanocomposite Coatings grown by PVD Magnetron Sputtering

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The increasing prevalence of nosocomial infections, particularly those associated with surgical sites, necessitates the development of advanced antimicrobial coatings for surgical tools and implants. This study focuses on the surface modification and characterization of a nanocomposite layer comprising AgO/AgTaO/TaO on SS 316 L stainless steel using Physical Vapor Deposition (PVD) magnetron sputtering. The AgO/AgTaO/TaO coating aims to enhance the physicochemical, mechanical, and biological performance of the substrates. The thin films were annealed at 450°C and 750°C to study the effects of temperature on their properties. Characterization techniques, including Field Emission Scanning Electron Microscopy (FESEM), Energy-Dispersive X-ray Spectrometry (EDX), Atomic Force Microscopy (AFM), and X-ray Diffraction (XRD), were employed to analyze the surface morphology, elemental composition, and crystallinity of the coatings. Results showed that annealing at 450°C produced a smooth surface with a roughness of 0.107 nm and initiated TaO crystallization, while annealing at 750°C led to silver segregation and increased surface roughness. These findings suggest that the annealing temperature critically affects the coating's properties, potentially impacting its effectiveness in preventing bacterial adhesion and biofilm formation. The study underscores the potential of AgO/AgTaO/TaO nanocomposite coatings in improving the safety and performance of surgical tools and implants.

1. Introduction

Bioinert metals are mainly used for replacing broken or damaged hard tissues in medical applications [1]. SS 316 L has received the highest demand for surgical tools among these biomaterials due to its high corrosion resistance, good strength, and ability to withstand high temperatures. It also has a high melting point at around 2,500 degrees Fahrenheit [2].

Nosocomial infections, also known as healthcare-associated infections, are a leading cause of complications and fatalities linked to infectious diseases. These infections can arise in various parts of the body, including the bloodstream, urinary tract, and particularly at surgical sites [3]. The latter are particularly vulnerable to bacterial colonization and biofilm formation, as the presence of foreign materials can impair the immune system's response. HAIs are linked to approximately 100,000 deaths annually in North America [4]. The transmission of these infections is often related to healthcare products and services, representing a critical area for improving patient safety and outcomes. Surgical tools and implants can act as carriers for bacteria that cause infectious diseases. Bacterial biofilms, which form under stress conditions, are especially challenging to eradicate. Prevention of their growth is the most effective strategy because biofilms tend to resist antibiotic treatments, rendering such approaches ineffective [5,6]. Instead, surfaces designed to prevent bacterial adherence and growth offer the best defense against infection [7,8]. The development of hygienic coatings for healthcare products is therefore a significant area of research, aimed at preventing infection transmission, enhancing patient health, saving lives, and reducing costs [9,10].

These antimicrobial coatings must possess qualities such as optimal microstructure, strong adhesion, the right surface roughness, hydrophobic properties, and thermal stability [11,12] The process of steam sterilization, which exposes surgical tools to temperatures of 121°C for 24 minutes, is a standard procedure to eliminate microorganisms [13]. Tantalum oxide has emerged as a promising biomaterial due to its excellent blood compatibility, cytocompatibility, and antibacterial properties [14]. Its wide bandgap is crucial for its antithrombotic performance, which is highly effective against blood clotting [15]. TaO is becoming a favored coating material for stainless steel 316 L and titanium-based blood-contact devices, like stents. Silver, recognized for its potent antibacterial action for centuries, has been used to treat infections and burns. Silver ions target and deactivate bacterial surface proteins [16]. While Ag is generally safe for biomedical applications, concern arises with exposure to high concentrations on open wounds, potentially causing argyria [17]. In a recent study by Yontar et al., the study found that by increasing the proportion of nano-silver in coatings, bacterial proliferation was significantly diminished, by a factor of up to 100. Additionally, toxicity assessments indicated that these nano-silver-infused were not harmful to live HaCaT skin cells and A549 lung cancer cells [18]. However, silver nanoparticles have been noted to be cytotoxic at higher concentrations, likely due to their small size and unique properties [19,20].

In this study, a nanocomposite layer composed of AgO/AgTaO/TaO has been developed on SS 316 L for improving the physicochemical, mechanical and biological performance of surgical tools and implants using Physical Vapor Deposition (PVD) magnetron sputtering. PVD magnetron sputtering offers several distinct advantages over other coating techniques. It can produce thin films with exceptional uniformity, smoothness, and high purity. Additionally, it allows for precise control over deposition parameters, enables the possibility of in-situ reactions, and results in coatings with excellent mechanical performance [21]. A poorly crystallized tantalum oxide (TaxOx) layer exhibits low hardness and adhesion strength, which contribute to coating delamination. However, in this study, both 450 and 750℃ conditions are favorable for targeted application. For AgO/AgTaO/TaO annealed at 450℃, crystallized tantalum oxide was achieved. For AgO/AgTaO/TaO annealed at 750℃, although some Ag which is softer than TaO migrates to the surface associated with TaO, the migrated silver naturally tends to crystallize into a face-centered cubic (FCC) structure. Furthermore, the smooth surface morphology (0.107 nm) was obtained at 450℃ annealing temperature which much lower than similar previous works.

2. MATERIALS AND METHODS

The Kurt J. Lesker Company provided the tantalum (Ta) and Ag PVD targets, which were 99.99% pure. These targets had a diameter of 101.6 mm and a thickness of 3.1 mm. Stainless steel (SS) 316 L substrates, measuring 20 × 10 × 2 mm, were ground using silicon carbide (SiC) paper with grits ranging from 1500 to 2500. The substrates were polished to a mirror-like finish using a 3 mm polycrystalline diamond suspension. After polishing, the substrates were washed with distilled water and dried with blown air. Subsequently, the specimens underwent ultrasonic cleaning in acetone followed by ethanol for 10 minutes each, and were then dried at room temperature.

A. Experimental Procedures

A PVD (TF450 Sputtering System, SG Control Engineering Singapore) series magnetron sputtering system was used to deposit AgO/AgTaO/TaO thin films. The prepared specimens were placed in the deposition chamber of the PVD magnetron sputtering system. The base pressure of the chamber was evacuated to approximately 2.67 x 10^{-3} Pa. The variables for magnetron sputtering were set according to Table 1. To reduce contamination in the vacuum chamber, the surface of the target was pre-sputtered under Argon gas before deposition. O2 was introduced to form an Ag-containing ceramic layer on the substrate using reactive magnetron sputtering, as described in previous work. The distance between the substrate and the targets was maintained at 15 cm. A zero bias voltage was applied to the substrates, while Ta and Ag targets were powered with DC and RF powers, respectively.

The thin film deposition was conducted for 120 minutes, maintaining a working pressure of around 1.19 Pa. After deposition, the specimens were removed and stored in a dry box for further processing and characterization. Thermal/annealing treatment was performed at 450°C for 60 minutes in a tube furnace, with a heating rate of 2°C/min. All samples were held at 200°C for homogenization.

TABLE I EXPERIMENTAL SETUP OF THIN FILM DEPOSITION BY PVD

Magnetron sputtering variable factor	Capacity
Power	200 W
Argon flow rate	45 sccm
Oxygen flow rate	6 sccm
DC Bias	0

Time	140 min (40, 20/40, 20)

B. Characterization

The microstructural and elemental characterization of the developed layers was carried out using Field emission scanning electron microscopy (Thermo Fisher Scientific Quattro ESEM, United States) and Energy-dispersive X-ray spectrometry (EDX). Furthermore, the extended surface topography was measured by non-contact mode of Atomic Force Microscope (PARK NX 10, Korea). The phase identification was performed by X- ray diffractometer (XRD, PANalytical Empyrean, Netherlands) using a Cu-Ka radiation. The operating voltage and current were set to be 40 kV and 40 mA respectively over a 2h range of 10–90˚.

3. RESULTS AND DISCUSSION

A. FESEM Microstructural Analysis

The thin film surface of the as-grown AgO/AgTaO/TaO appeared glossy black. Nevertheless, this early appearance faded to shiny blue after annealing at 450℃ and turned pale brown at 750℃ annealing. Figure 1(a–c) presents the FESEM microstructural analysis of as-grown and annealed AgO/AgTaO/TaO thin film. Meanwhile, Figure 1 displays its elemental composition. Figure 1 illustrates the as-grown AgO/AgTaO/TaO thin film. A nicely distributed AgO/AgTaO/TaO nanocomposite was observed with a few TaO crystals at the surface, suggesting that the surface coating dominantly covered the TaO outer layer. The EDX results in Figure 1 support this.

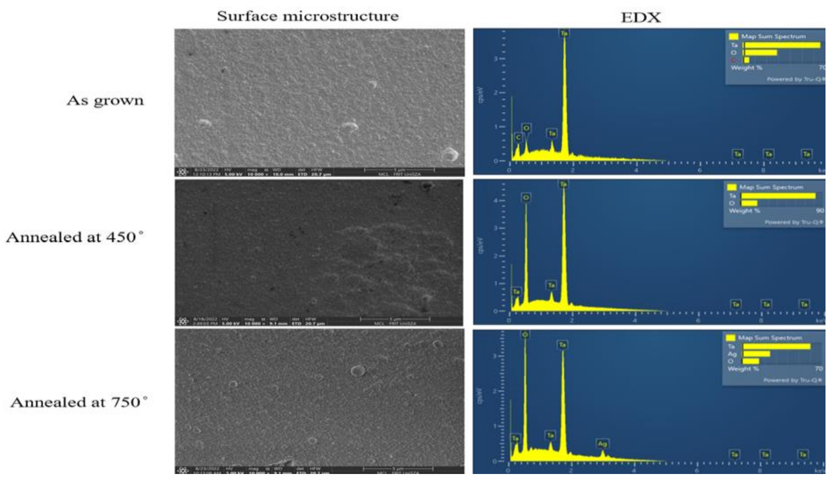

Fig. 1 FESEM surface morphology of as-grown, annealed at 450 and 750℃ and its EDX analysis of AgO/AgTaO/TaO thin film

When this nanocomposite is annealed at 450°C, only the TaO top layer responds, initiating TaO segregation. The particle size exhibits dynamic changes, expands and then flattens toward the surface, reducing particle height. At elevated temperatures, atomic mobility increases, allowing tantalum and oxygen atoms to migrate more freely. This unstable state of thermodynamics in tantalum oxide composition triggers the segregation to the surface to minimize the system's free energy. This kind of TaO segregation on the surface has been observed by several researchers [22]. After annealing at 750℃ of tantalum oxide's crystallization [23], it is suggested that the Ag from the inner AgO/AgTaO layer comes out after gaining stronger kinetic energy. This does not happen at 450℃ because Ag may not have enough thermal energy to overcome the barrier for surface segregation [24]. At higher temperatures of 750°C, the thermodynamic stability changes, and Ag, which has a lower surface energy than tantalum oxide, becomes more thermodynamically favorable on the surface. The effect of annealing temperature on the TaO flatten and Ag segregation to the surface has been confirmed with the help of EDX, as presented Figure 1.

B. Surface Topography by AFM

The surface topography of all the developed layers was analyzed using atomic force microscopy (AFM) measurements. Figure 2 illustrates the AFM view of the as-grown, annealed at 450 and 750℃ of AgO/AgTaO/TaO with the surface roughness, Ra of 0.293, 0.107 and 0.260 nm, respectively. The AFM surface topography is very much in agreement with the topographic features visible in FESEM image shown in Figure 1. The as-grown AgO/AgTaO/TaO presented the 0.293 nm of surface roughness (R_a) value. However, the R_a value decreased to 0.107 nm after AgO/AgTaO/TaO was annealed at 450℃, which is in line with the expanding flattening phenomenon. Then, the R_a value rose to 0.260 nm when AgO/AgTaO/TaO annealed at 750℃. Upon exposure to the heating during annealing at 750℃ peak height, surface roughness increases due to the Ag segregation as visible in Figure 1.

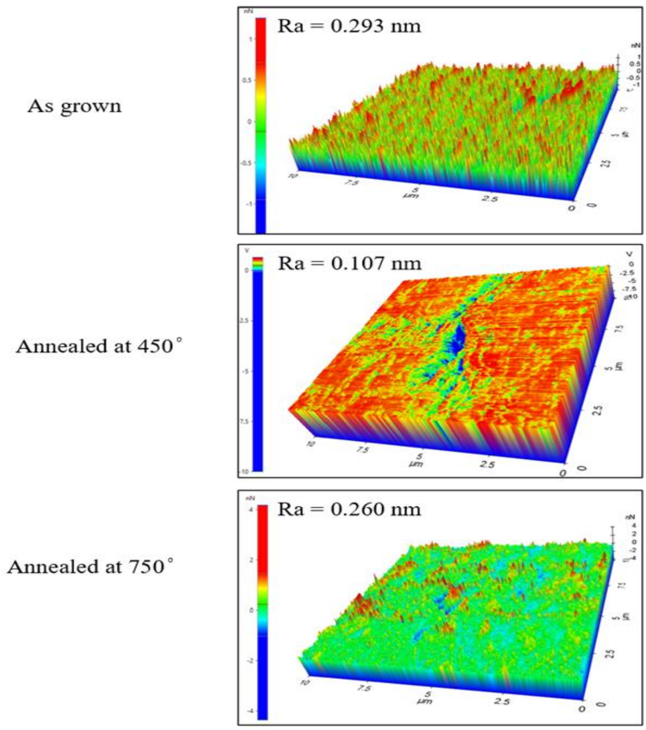

Fig. 2 AFM 3 D view of the as-grown, annealed at 450 and 750℃ of AgO/AgTaO/TaO thin film

C. Phase Analysis by XRD

XRD has been used to analyze the developed composite layers. As depicted in Figure 3, the as-grown AgO/AgTaO/TaO layer showed the presence of Ag (PDF 01-087-0717), Ag_2O (98-002-0368), and Ta_2O (98-002-8387) on the surface. Ag peaks appeared at positions 2θ of 38.12, 44.31, 64.45 and 77.1 ° with orientations of cubic crystal planes (1 1 1), (2 0 0), (2 2 0) and (3 1 1), respectively. Ag_2O diffracted at 33.59 and 38.36° at (1 0 0) and (0 1 1) planes. Ta_2O at 38.03 and 68.7° at (0 2 2) and (2 2 4) planes.

After annealing at 450℃, the Ag peaks remain at the same position. However, a new Silver Oxide phase forms. The Ag_2O_2 and Ag_3O_4 reflected at positions 2θ of 37.18 (1 1 1) and 37.20 (1 1 -2) consistent with the standard data file PDF 01-084-1547 and PDF 00-040-1054. When annealing up to 750℃, only Ag peaks appeared at positions 2θ of 44.31°. These XRD results are in line with those obtained in FESEM-EDX and AFM.

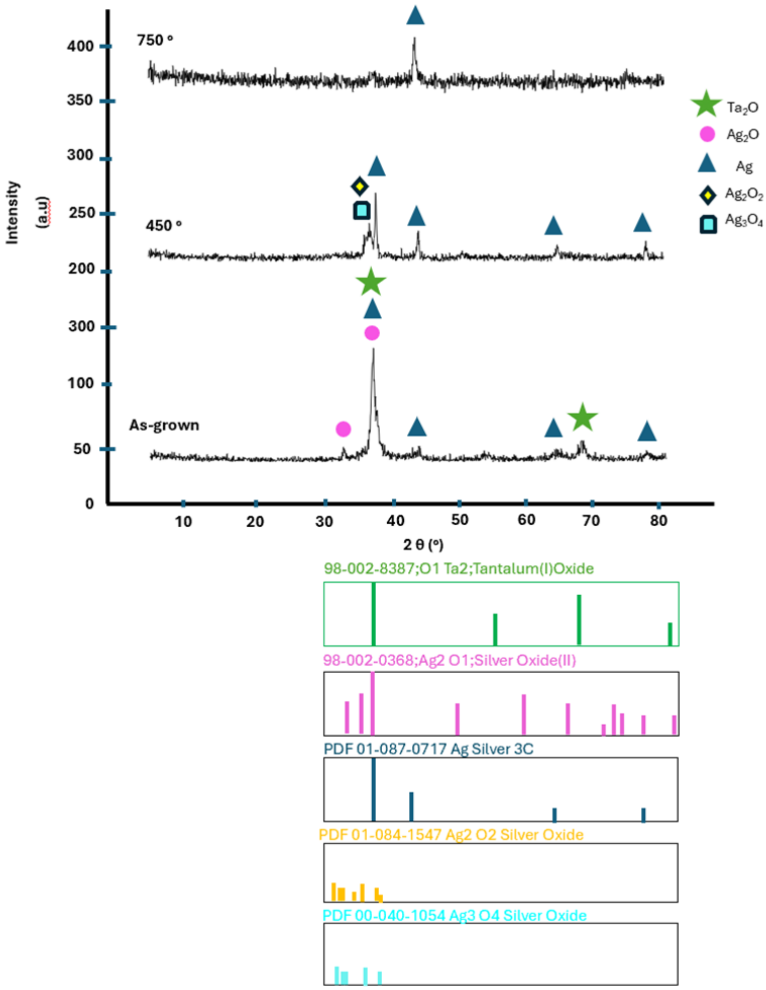

Fig. 3 XRD patterns of the as-grown, annealed at 450 and 750℃ of AgO/AgTaO/TaO thin film

4. CONCLUSIONS

1) A nanocomposite multilayer of AgO/AgTaO/TaO has been successfully developed on SS 316 L for surgical and implant applications using PVD magnetron sputtering. The as-grown thin film layer exhibited a smaller TaO particle size due to the stability of the thermodynamic state, which resulted from the low kinetic energy of the coating system.

2) However, annealing at 450 and 750℃ allows the unique characteristic of trilayer AgO/AgTaO/TaO composite as proved by FESEM-EDX, AFM and XRD characterizations. After the 450℃ annealing, the TaO particle at top layer gains more kinetic energy, which may lead to the TaO's expansion followed by spreading across the surface, leading to a decrease in surface roughness.

3) The surface morphology evaluation found a very smooth 450℃ annealing AgO/AgTaO/TaO coating (0.107nm), which is favorable for surgical and implantation tools.

4) Beyond the TaO crystallization point, 750℃ annealing temperature promotes the Ag mobility to the surface which is responsible for the increasing surface roughness value (0.260 nm). A higher diffusion coefficient indicates that Ag atoms can move more rapidly through the lattice AgO/AgTaO/TaO system to achieve thermal stability. This interesting finding suggests the need for a detailed study on the effect of annealing temperature on physicochemical, mechanical and biological behaviour of tri-layer AgO/AgTaO/TaO composite.

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