Antibacteria and anti-wear TaN–(Ag,Cu) nanocomposite thin films deposited on polyether ether ketone


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Hard TaN–(Ag,Cu) nanocomposite films were deposited on PEEK (polyether ether ketone) substrates using reactive co-sputtering. The films were then annealed using RTA (Rapid Thermal Annealing) at 200 °C to induce the nucleation and growth of soft metal particles in the TaN matrix and on the surface of the films. After examining the surface morphologies, structures, and mechanical properties of the samples, they were tested for their tribological properties under a normal load of 1 N or 5 N. It was found that the samples’ tribological properties were much improved compared to uncoated PEEK, even though the substrate is relatively soft. This was especially apparent for heavier loads. Apparently, the solid lubricants (i.e., Ag and Cu particles) that emerged on coating’s surface during the annealing process reduced the frictional force and wear rate of PEEK. These results were similar to those that were obtained using tool steel substrates. The coated samples were also tested for their anti-bacterial properties using Gram-negative Escherichia coli (E. coli) and Gram-positive Staphylococcus aureus (S. aureus) bacteria. It was found that the anti-bacterial efficiency of these samples was significant against both E. coli and S. aureus, even though the deposited samples were annealed through RTA at the relatively low temperature of 200 °C. There was no peeling found between coatings and PEEK substrates after tribological and scratch tests.

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1. Introduction

PEEK (polyether ether ketone) is a semicrystalline thermoplastic with good mechanical and chemical resistance properties. It is widely used in the aerospace, automotive, and chemical-processing industries. PEEK is currently considered to be one of the best potential substitutes for metal alloys in surgical implants. This material has a desirable combination of high strength, stiffness, and resistance to fatigue [1,2]. It is also non-toxic and has natural radiolucency [3]. In particular, PEEK has an elastic modulus around 5 GPa, which is very similar to that of human bone, while the elastic modulus of a metal alloy is approximately 20 times greater than that of bone [2,4]. However, when compared with metal alloys or ceramics, PEEK has relatively low wear resistance, which is a disadvantage as wear debris could cause serious problems if PEEK were to be used in a common surgical implant [3]. Furthermore, PEEK does not show detectable antibacterial behavior, which means that the use of PEEK in surgical implants may lead to certain infection [4]. Therefore, it is of interest to improve PEEK by depositing a thin film on its surface, lowering its friction force and improving its antibacterial behavior. A low-temperature physical-vapor-deposition process can be adopted to achieve this goal. Previous studies have proven that TiN, Al2O3, and diamond-like carbon coatings can be deposited on polymeric materials, thus improving their tribological properties [5,6]. It has also been shown that doping Ag and/or Cu in hard coatings may further improve the coatings’ anti-bacterial behaviors while maintaining a satisfactory elastic modulus and lowering the materials’ friction coefficient [7]. A recent study on a similar concept focused on adding zinc oxide particles to PEEK, forming a new grade of nanocomposite material. This nanocomposite had enhanced mechanical properties as well as much improved antibacterial behavior [8,9].

In the past, tantalum nitride thin films doped with soft metals (i.e., TaN–Cu, TaN–Ag, and TaN–(Ag,Cu)) have been prepared using a hybrid process that starts with reactive co-sputtering, which is followed by rapid thermal annealing (RTA) at a temperature higher than 350 °C [10–12]. Tantalum metal and alloys are known to have excellent bio-compatibility, which makes TaN an excellent choice of protective coating in bio-related applications [13]. Cu and Ag, as doping elements, are have been proven to be immiscible with TaN, making the synthesis of TaN–Cu, TaN–Ag, or TaN–(Ag,Cu) nanocomposite thin films possible [12,14]. In particular, incorporating both Ag and Cu into TaN has some advantages over incorporating just Ag or Cu.
These advantages include: (a) similar or better tribological behaviors, (b) broader spectrum of bactericide, (c) accelerated dissolution rates of metal ions, and (d) lower annealing temperature. In the case of TaN–(Ag,Cu), the annealing temperature can be lowered down to 200 °C [13]. With this annealing temperature, the preparation of annealed TaN–(Ag,Cu) nanocomposite films deposited on PEEK becomes possible. Furthermore, it has been reported that Ag ions have strong bactericidal effects on more than 16 species of bacteria, while Cu ions may be effective against other groups of bacteria [4,15,16]. Thus, producing Ag–Cu-based inorganic anti-bacterial agents leads to a wider spectrum of bactericidal effects [15,16].

The present study is aimed at improving the wear resistance and anti-bacterial properties of soft PEEK substrates by depositing TaN–(Ag,Cu) nanocomposite films on these substrates. These samples were then annealed at 200 °C through RTA. Afterwards, the mechanical and antibacterial properties of these samples were examined in order to see if the films improved the PEEK’s properties as theorized.

2. Experimental methods

TaN–(Ag,Cu) thin films were deposited on PEEK substrates with the surface dimensions of 2 cm × 2 cm (Grade 450G, GLAI Enterprises Ltd.) using reactive co-sputtering with Ta, Ag, and Cu targets. Each target had a diameter of 50 mm and was tilted by 30°. The distance of target-to-target and target-to-substrate was 150 mm and 100 mm respectively. For deposition, the sputtering system was first pumped down to 7 × 10⁻⁴ Pa. Then, Ar gas (35 sccm) was introduced to fill the chamber up to 0.65 Pa. During deposition, the power of Ta was kept at 170 W, while the power of Ag was set at 20 and 35 W (RF) and the power of Cu was set at 14 and 18 W (DC), in order to prepare films containing 2 and 7 at.% soft metals (i.e., Ag and Cu). The atomic ratio of Ag to Cu was 65% to 35%. N₂ gas was added at 4.5 sccm in order to produce stoichiometric TaN. During deposition, the substrate was biased with 40 W (RF) without additional heating. The substrate temperature was measured to be less than 100 °C. The total thickness of these films was about 1 μm, including an interfacial Ta/TaN layer that was 50/150 nm thick. Deposition rate was measured to be 12.5 nm/min for TaN–(Ag,Cu), 12 nm/min, and 16 nm/min for Ta. Some of the deposited films were then annealed at 200 °C for 2, 4, 8, and 20 min using an RTA system (Sj, ARTS-150) with ramping rate of 100 °C/s. The flow rate of Ar was fixed at 2000 sccm during RTA. Further procedure details may be found in Refs. [10,11].

The mechanical properties (i.e. hardness and Young’s modulus) of the films were characterized using a Hysitron triboindenter (TI-900) equipped with a Berkovich tip. Prior to the tests, the tip was carefully calibrated using the standard procedure documented by Oliver and Pharr [17]. According to Chen and Bull [18], when using a Berkovich indenter with a tip rounding less than 100 nm, the suggested indentation penetration for most coated systems (including very hard coatings on soft substrates) should be less than one-tenth of the coating thickness in order to minimize the substrate effect. This principle was adopted when carrying out the nano-indentation tests on our samples. In this study, the displacement control mode was used to achieve the maximum indentation depth of around 70 nm in order to minimize the substrate effect. The loading rate was 1 nm/s. Eight indentation tests were performed on each sample. The hardness and reduced modulus were determined using the Oliver and Pharr method [17], which is a reasonable approximation as PEEK has relatively insignificant viscoelastic behavior at the temperature of measurement (i.e., room temperature) [19]. To calculate Young’s modulus, a Poisson’s ratio of 0.15 [20] was used.

In order to investigate the surface metal particles and film morphology, the sample films were examined using field-emission scanning electron microscopy (SEM) (15 kV, JEOL 6700F). The phases of the deposited films were studied using the X-ray diffraction (XRD) technique. Using these examination methods, we were able to confirm the formation of Ag/Cu phases after annealing. The X-ray diffractometer (Philips PW 1830) used monochromatic high intensity Cu Kα radiation (λ = 0.1541 nm). The scanning angle was from 25° to 65° with a step size of 0.04° and a measuring time of 1.60 s per step.

For wear-resistance testing, a pin-on-disc apparatus was used. This apparatus consists of a pin with an alumina ball (6.35 mm in dia.) on the point. This pin was placed perpendicular to the coated substrates. The disc was made to rotate beneath the alumina ball at a speed of 12 cm/s under a load of 1 or 5 N. The total sliding distance was 500 meters. After the test, the friction coefficient was determined and the wear tracks of each coating were measured using a surface profiler (Surfcofer, Kosaka). The wear rate of the sample was evaluated by calculating the volume of the wear track and then dividing the volume by sliding distance. For the adhesion examination, scratch testing was carried out using a normal load that varied from 0 to 40 N.

For the antibacterial testing, the coated and uncoated PEEK samples (2 cm × 2 cm) were placed on a tray and then incubated at 37 °C with a calibrated bacterial suspension of Gram-negative Escherichia coli (E. coli) and Gram-positive Staphylococcus aureus (S. aureus) at 1 × 10⁶ CFU. After incubation, the Antibacterial Efficiency (E) of each sample was evaluated using the following equation:

$$E(\%) = \frac{|A-B|}{A} \times 100\%$$

where A = the number of viable bacteria on the uncoated (standard) sample in the tray; and B = the number of viable bacteria on the coated sample in the tray. Three sets of uncoated and coated samples were incubated with the bacterial suspension. The antibacterial efficiency was calculated for each set and then averaged to obtain the final result.

3. Results and discussions

3.1. Structural analysis

The X-ray diffraction patterns of the TaN–(Ag,Cu) films after being annealed at 200 °C for varying times are presented in Fig. 1. It can be observed that the as-deposited film only shows the diffraction peaks of the TaN phase. The Ag and Cu peak intensities become stronger as
the annealing time is increased, which means the Ag and Cu particles are emerging and becoming larger as the annealing time is increased.

Fig. 2 shows the surface and SEM micrographs of the TaN–(Ag,Cu) nanocomposite films after being annealed at 200 °C for 2 and 8 min. The Ag and Cu particles that emerged during the annealing process can be observed on the films’ surface. The particle size (10–100 nm) is smaller than the sizes reported on Si substrates, which were treated at a higher temperature [21]. This is apparently due to the difference in annealing temperature. Fig. 3 shows the cross-sectional SEM micrographs of the samples before and after annealing for 4 min. It can be seen that the films are dense and adherent to the PEEK substrate both before and after annealing. The results of the varying-load scratch testing (not shown) do not show any sign of film detachment.

3.2. Mechanical and tribological properties

Fig. 4 shows hardness and modulus values of TaN–(Ag,Cu) films before and after being annealed at 200 °C for 4 min. It can be observed that both the hardness and modulus increased for coated PEEK. Here, the hardness and modulus of substrate (PEEK) is around 0.47 and 5.36 GPa respectively, and its glass transition temperature is around 149 °C. After annealing, the hardness was further increased, while the modulus was decreased. This implies the increase of crack-growth resistance (H/E²) after annealing. It can be stated that the mechanical properties of the PEEK were greatly improved after the coating was applied. The hardness and modulus values of the TaN–(Ag,Cu) films are higher than the hardness and modulus values of the TaN film (around 20 GPa). This is due to the incorporation of soft metals and the toughening mechanisms used [22]. It is normally difficult to deposit a hard coating on soft substrates. However, the results obtained from during this study from tribo-testing show promising results, mainly due to the emergence of Ag and Cu particles as noted above. The Ag and Cu particles function as solid lubricants, resulting in low friction force and, thus, a lowered wear rate.

Furthermore, the toughness of MeN-soft metal films can be improved through the formation of soft metal networks [22]. Fig. 5a and b show the wear rates and friction coefficients of un-annealed and annealed TaN–(Ag,Cu) (2 and 7 at.%) coated PEEK. The rates shown were obtained through tribo-testing under a 1 N normal load. These low friction coefficients are due to the lubricious soft metals which were smeared in the wear tracks. This can be easily proven by observing the wear tracks left on the uncoated PEEK and TaN–(Ag,Cu)-coated samples, as seen in Fig. 5c and d. The wear track left on the uncoated PEEK sample has no trace of soft metals which could have functioned as solid lubricants to help reduce friction. Consequently, the uncoated sample has a high friction coefficient (1.2) and wear rate (1 × 10⁻⁵ mm³/m).

However, in the TaN–(Ag,Cu)-coated samples, the friction coefficient was 0.5, while the wear rate was to 0.4 × 10⁻⁵ mm³/m, both decreases from the friction coefficient and wear rate of the uncoated sample. Fig. 6 shows the friction coefficients and wear rates of un-annealed and annealed TaN–(Ag,Cu) (2 and 7 at.%) coated PEEK. For these tests, the normal load was set at 5 N. The coated and annealed sample that contains...
7 at.% Ag–Cu shows the lowest friction coefficient (and, thus, the lowest wear rate), even when compared to the tests carried out with a 1 N normal load. It was thought that, under a 5 N normal load, the contact area would increase due to the softness of PEEK. In this case, the increased contact area meant that the amount of contacted solid lubricants (soft metal amount) also increased. Thus, the friction and wear rate are lower. These results are different from those obtained when the substrate was made of tool steel. In the case of coated tool steel, the friction and wear rate increased with the increase of the normal load.

### 3.3. Anti-bacterial behaviors

The antibacterial efficiency as a function of annealing temperature against *E. coli* and *S. aureus* is shown in Fig. 7. According to these figures, the TaN–(Ag,Cu)-coated PEEK samples, which were annealed at the relatively low temperature of 200 °C, increased in antibacterial efficiency against *E. coli* and *S. aureus* as annealing time increased. This is because the annealing time is what determines the exposed amount of Ag and Cu particles. Once dissolved, these particles generate Ag and Cu ions that then destroy the membranes of bacteria that come into contact with the surface. Fig. 8 shows the SEM images of *E. coli* and *S. aureus* before and after being exposed to a buffer solution that contains Ag and Cu ions. The annealed TaN–(Ag,Cu)-coated PEEK shows good anti-bacterial behaviors against both of these bacteria. As predicted, increasing the annealing time increases the amount of exposed Ag and Cu, thus increasing antibacterial efficiency. By comparing the graphs shown in Fig. 7, it can be observed that the annealed samples are more efficient against *E. coli*. This can be explained by the fact that, when annealed at low temperatures, Ag particles emerged on the surface of the coated samples more quickly than Cu particles did [21]. As has been reported previously, Ag is more efficient against *E. coli* than *S. aureus*, resulting in...
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ciency noted above. In sum, these results are as signif-

icant as those obtained from coated hard substrates annealed at 350 °C

and above.

4. Conclusions

Adherent TaN–(Ag,Cu) nanocomposite thin films were deposited on
PEEK substrates using a hybrid method that combined reactive co-
sputtering and rapid thermal annealing, in order to reduce the friction
coefficient and wear rate of PEEK as well as enhance the substrates’ an-
tibacterial efficiency. Ag and Cu nano-particles, acting as solid lubricants
as well as antibacterial agents, emerge on the surface of the samples
after they were annealed at 200 °C for times varying between 2 and
8 min. The tribological properties of TaN–(Ag,Cu) coated PEEK improve
as annealing time increases. This is due to the fact that those emerged
soft metal particles could be smeared out and function as ef

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solid lubricants. After being annealed, the TaN–(Ag,Cu)-coated PEEK
samples showed the lowest friction coefficient and wear rate even
when the normal load was increased from 1 N to 5 N. This could be at-
tributed to the fact that the increased contact area of the testing appara-
tus to the sample meant there was increased contact to solid lubricants
(soft metal particles) on the samples’ surface. It was also found that the
antibacterial efficiency of these samples against E. coli and/or S. aureus is
as significant as the efficiency obtained using other substrates annealed
at temperatures higher than 350 °C. The reduction of annealing tempera-
ture is quite meaningful in terms of future applications of anti-bacteria
and anti-wear coatings on polymeric materials.

Fig. 6. Wear rate and friction coefficient of PEEK for (a) TaN–(Ag,Cu)-2 at.% and (b) TaN–(Ag,Cu)-7 at.%-coated PEEK under 5 N load.

Fig. 7. Time evolution of antibacterial efficiency of TaN–(Ag,Cu) thin films against E. coli and S. aureus for samples annealed at 200 °C for various annealing time: 2 at.% Ag–Cu ((a) and (c)), and 7 at.% Ag–Cu ((b) and (d)).
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References


Fig. 8. SEM images of (a) E. coli without contact with TaN–(Ag,Cu), (b) E. coli contacted with TaN–(Ag,Cu), (c) S. aureus without contact with TaN–(Ag,Cu), (d) S. aureus contacted with TaN–(Ag,Cu).
