Plasma sprayed alumina–nanosilver antibacterial coatings

Jinjin Gao,a Chunxia Li,*b Jingfang Zhou,c Liqiang Lu,a Chengjian Zhao b and Yingchun Zhu*a

Alumina coatings have wide-ranging applications by virtue of their inherent wear and corrosion resistance and attractive dielectric and diffusion barrier properties. In many cases, they do not meet the antibacterial demand to eliminate microbiologically-induced corrosion and diseases. The aim of this work is to prepare plasma sprayed alumina–nanosilver (Al2O3/Ag) coatings and investigate their antibacterial properties with various compositions. Moreover, Al2O3/Ag coatings are optimized to use minimum amounts of silver nanoparticles (AgNPs) and exhibit excellent antibacterial properties. Al2O3 coatings with five different amounts of AgNPs were deposited on titanium alloys substrates by plasma spray. The Al2O3/Ag coatings, which were denoted as A1, A2, A3, A4 and A5, were prepared by using α-Al2O3 powders containing 1 ppm, 10 ppm, 100 ppm, 1000 ppm and 10 000 ppm AgNPs, respectively. The composition and morphology of Al2O3/Ag coatings were investigated by X-ray diffraction and scanning electron microscopy. The antibacterial activity of Al2O3/Ag coatings was tested using Escherichia coli (E. coli) and Staphylococcus aureus (S. aureus) as model strains of Gram negative and Gram positive bacteria, respectively. The bacterial adhesion was also examined by employing both of the bacteria to observe bacterial adhesion status and evaluate antibacterial property of as-prepared coatings. The results showed the Al2O3/Ag coatings with more than 10 ppm AgNPs exhibited strong antibacterial property against E. coli and S. aureus. Bacterial adhesion assays showed that A2–A5 had anti-adhesive property of E. coli and S. aureus, which was in accordance with the antibacterial results. Moreover, the main factors influencing the antibacterial properties of Al2O3/Ag coatings were discussed with silver nanoparticles and hydrophobicity of the coatings.

1. Introduction

Alumina coatings have been widely used for anti-wear and anti-corrosion applications due to their high hardness, chemical inertness and high melting point, as well as to their high resistance to abrasion and erosion.1,2 Although Al2O3 coatings are selected for their favourable mechanical properties, they do not meet the requirement of antibacterial behaviour, which has limited their application in microbiologically influenced corrosion, water treatment industry and environmental protection etc. Therefore, considerable efforts have been made to develop the antibacterial properties of Al2O3 coatings.1,3

Al2O3 coatings could be prepared by techniques such as chemical vapour deposition (CVD), physical vapour deposition (PVD), sol–gel, plasma electrolytic oxidation (PEO) and plasma spray.3 Among these techniques, plasma spraying is one of the most extensively used techniques to deposit Al2O3 coatings on metal substrates at a low cost and high deposition rate.6,7 In various crystal phases for Al2O3, the α-Al2O3 has long been one of the most widely used industrial ceramics due to its combination of physicochemical performances such as great wear resistance, high melting point and good thermal and chemical stabilities.8 The mechanical properties of α-Al2O3 with the rhombohedral structure are conspicuously better than those of γ-Al2O3 with cubic structure.9 Therefore, alumina coatings were tentatively prepared by using α-Al2O3 powder feedstock with proper plasma spray technique.

The outbreak of infectious disease generally poses a serious threat to public health all over the world, especially with the emergence of antibiotic-resistant bacterial strains.10 Therefore, there is a great demand for Al2O3 coatings with antibacterial properties. Although various methods such as adding antibiotics and organic antibacterial agents into the coatings have been used to prepare antibacterial coatings,11 there is growing interest in incorporating inorganic antibacterial agents reducing the infection rate, while exhibiting a broad spectrum of antibacterial activities.12,13 A number of nanoparticles such as...
Ag, Cu, Zn and Au have been studied as inorganic antibacterial agents. Compared with other nanomaterials, silver nanoparticles have attracted increasing attention because of other benefits such as high chemical activity, non-cytotoxicity at suitable doses, and smaller possibility to develop resistant strains. So it is possible to fabricate antibacterial alumina coatings by introducing silver nanoparticles into the $\alpha$-$\text{Al}_2\text{O}_3$ powders. It is suggested that nanoscale Ag at higher levels could induce toxic. Vik et al. pointed that the maximum silver concentration released in vitro should be no more than 10 ppm. Therefore, it is significant to prepare $\alpha$-$\text{Al}_2\text{O}_3$ coatings with excellent antibacterial property and suitable AgNPs doses.

In our work, $\alpha$-$\text{Al}_2\text{O}_3$ coatings with different amounts of silver nanoparticles were deposited on titanium alloys substrates by plasma spray. The $\alpha$-$\text{Al}_2\text{O}_3$/Ag coatings were prepared by using $\alpha$-$\text{Al}_2\text{O}_3$ powders containing 1 ppm, 10 ppm, 100 ppm, 1000 ppm and 10 000 ppm AgNPs, respectively. This work aimed to investigate the effects of composition on antibacterial property and obtain a material with minimum amount of AgNPs as well as maintaining the excellent antibacterial property.

2. Materials and methods

2.1 Preparation of alumina–silver coatings

Commercial $\alpha$-alumina powders (99.999 wt%) with an average size of 20–50 $\mu$m (Jing Rui New Material Co. Ltd) and silver powders (99.5%) with an average size of 60–120 nm (Aladdin Chemistry Co. Ltd) were employed as raw powders for resulting coatings. The process of manufacturing spray powders can be described as follows: firstly, the original $\alpha$-$\text{Al}_2\text{O}_3$ powders were sintered in a muffle furnace to increase the bonding strength and make organic binder volatilize, the sintering system was presented in Table 1. Secondly, the sintered $\alpha$-$\text{Al}_2\text{O}_3$ and Ag powders were wet milling for 4 h in a ball mill. Thirdly, the mixed powders were sintered for 1 h at 800 °C in argon atmosphere. Lastly, the sintered powders were crushed and separated by 200 mesh and 400 mesh screens. The powders with a size between 200 and 400 mesh were used as feedstock material for plasma spray. In order to investigate the effect of content of silver nanoparticles in $\alpha$-$\text{Al}_2\text{O}_3$/Ag coatings on antibacterial properties, $\alpha$-$\text{Al}_2\text{O}_3$ powder mixed with various weight percentages of AgNPs were deposited with a proper spraying condition. In our study, five different kinds of $\alpha$-$\text{Al}_2\text{O}_3$/Ag coating samples were investigated. The $\alpha$-$\text{Al}_2\text{O}_3$/Ag coatings, denoted as A1, A2, A3, A4 and A5, were prepared by using $\alpha$-$\text{Al}_2\text{O}_3$ powders containing 1 ppm, 10 ppm, 100 ppm, 1000 ppm and 10 000 ppm AgNPs, respectively. For comparison, the plasma sprayed pure $\alpha$-$\text{Al}_2\text{O}_3$ coatings were also prepared under the same conditions to serve as control and denoted as A0.

A 2000 atmospheric plasma spraying equipment (Sulzer Metco, Switzerland) was used to deposit the $\alpha$-$\text{Al}_2\text{O}_3$/Ag coatings. Prior to depositing the coatings, the surface of the titanium alloys substrates with dimensions of $15 \times 50 \times 1$ (all mm) was thoroughly cleaned, degreased, and grit-blasted with corundum in order to produce a rough surface for good bonding. Coating samples were deposited onto the titanium alloys substrates by atmospheric plasma spray. The spray parameters were listed in Table 2.

2.2 Specimens analyses

The surface morphology of the $\alpha$-$\text{Al}_2\text{O}_3$/Ag and $\alpha$-$\text{Al}_2\text{O}_3$ coatings and the bacterial adhesion status on the coatings were observed by scanning electron microscopy (SEM, JXA-8100, JEOL, Japan and SEM, S-3400, JEOL, Japan). The compositions of the coatings were detected by X-ray diffraction (XRD, Ultima IV, Rigaku, Tokyo, Japan) with CuK$\alpha$ radiation. The hydrophobicity of the coatings and the substrates was measured using an automatic contact angle meter (SL200B, Solon, China).

The silver content in coatings was quantified by optical emission spectrometry (ICP-OES, 700 series, Agilent Technologies, USA) as following: alumina/silver powders were scrapped off from the $\alpha$-$\text{Al}_2\text{O}_3$/Ag coatings surface and weighed ($M$$_{coating}$), then dissolved in nitric acid solution. After the measurement of silver concentration ($C$$_{silver}$) in acid solution by ICP-OES, the silver in the coatings can be expressed as the value of ($C$$_{silver}$ $\times$ $V$$_{nitric~acid}$)/$M$$_{coating}$.

2.3 Antibacterial test

The antibacterial efficacy of the $\alpha$-$\text{Al}_2\text{O}_3$/Ag and $\alpha$-$\text{Al}_2\text{O}_3$ coatings was examined by counting method using Escherichia coli (E. coli, ATCC 25922) and Staphylococcus aureus (S. aureus, ATCC 25923). The coating specimens were sterilized by autoclave at 121 °C for 30 min after being cleaned in ethanol and deionized water. A volume of 100 μl of each strain (10$^6$ cfu (colony forming units) per ml) was dripped onto the surface of the samples. The specimens with the bacterial solution were incubated at 37 °C for 48 h in a constant temperature incubator and sterile water was also placed in the incubator to maintain high humidity (RH > 90%). Then, the specimens surfaces were scoured with sterile cotton swabs, washed-off with sterilized phosphate

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Sintering system of $\alpha$-alumina powders</th>
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<tr>
<td>Temperature/°C</td>
<td>Heating rate (°C min$^{-1}$)</td>
</tr>
<tr>
<td>0–200</td>
<td>10</td>
</tr>
<tr>
<td>200–400</td>
<td>6.7</td>
</tr>
<tr>
<td>400–600</td>
<td>5</td>
</tr>
<tr>
<td>600–1400</td>
<td>2</td>
</tr>
<tr>
<td>1400</td>
<td>0</td>
</tr>
<tr>
<td>1400–1600</td>
<td>2</td>
</tr>
<tr>
<td>1600</td>
<td>0</td>
</tr>
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<thead>
<tr>
<th>Table 2</th>
<th>Spray parameters of alumina–nansilver coatings</th>
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<tbody>
<tr>
<td>Current</td>
<td>600 A</td>
</tr>
<tr>
<td>Voltage</td>
<td>64 V</td>
</tr>
<tr>
<td>Powder feed rate</td>
<td>26 rpm</td>
</tr>
<tr>
<td>Spray distance</td>
<td>100 mm</td>
</tr>
<tr>
<td>Plasma gas Ar</td>
<td>40 slpm</td>
</tr>
<tr>
<td>Plasma gas H$\alpha$</td>
<td>12 slpm</td>
</tr>
<tr>
<td>Power carrier gas Ar</td>
<td>4.0 slpm</td>
</tr>
<tr>
<td>Angle of feed power</td>
<td>90°</td>
</tr>
</tbody>
</table>
buffer solution (PBS), and transferred into centrifuge tube. The centrifuge tube was shaken drastically for 5 min in order to make the bacteria enter into PBS thoroughly. The harvested bacterial solution was diluted in a sterilized PBS. These dilution series were then inoculated onto a standard agar medium and cultured at 37 °C for 24 h. The number of colonies formed on the agar was counted and five plates were assessed to obtain an average value. Control experiments were performed with bacteria solutions on Al2O3 coatings in the same conditions. The antibacterial ratio was calculated by the following formula:

\[
\text{Reduction in bacterial viability (％) = } \frac{(A - B)}{A} \times 100\%
\]

In our tests, where A and B correspond to the number of colonies calculated from the control and the testing sample.

2.4 Bacterial adhesion tests

Bacterial adhesion properties were tested on cultures of E. coli and S. aureus. Before the experiment, all the coating specimens were sterilized by autoclave at 121 °C for 30 min after being ultrasonically cleaned in ethanol and deionized water for 1 min. A volume of 100 μl of each strain \((1 \times 10^8 \text{ cfu ml}^{-1})\) was diluted in a sterilized PBS to the approximate concentration of \(10^6 \text{ cfu ml}^{-1}\). The coating specimens were placed in the 10 ml bacterial solution and incubated at 37 °C for 24 h on a rotary shaker. Specimens were rinsed three times gently in PBS to remove non-adherent cells and placed in glutaraldehyde (3% v/v) in PBS for 4 h to fix adherent bacteria. Next, the specimens were submersed in different ethanol/H2O solutions with increasing alcohol content (30%, 50%, 75%, 90%, 95% and 100% v/v) for 10 min, respectively. For the further dehydration, the samples were put in turn in hexamethyldisilazane–ethanol solutions at volume ratios of 1 : 2, 1 : 1, 2 : 1 and 1 : 0 for 10 min, respectively. Finally, the specimens were treated by air-dried and spray-gold. SEM was used to observe the bacterial adhesion status.

2.5 Silver release test

To examine the amount of released silver in deionized water, the Al2O3/Ag coatings tested were ultrasonically cleaned in deionized water for 1 min. Then each coating was immersed in 100 ml deionized water at 37 °C for 2, 5, 10, 15, 20, 25, 30 days. The concentrations variation of released silver was measured by atomic absorption spectrophotometer (AAS, 4510GF, Shanghai, China).

3. Results

Fig. 1 showed the surface morphologies of the plasma sprayed Al2O3 and Al2O3/Ag coatings. It can be seen that surface of the as-prepared coatings was rough and porous. All the coatings consisted of fully melted and the partially melted structure. Moreover, during the spraying process, some of the particles underwent melting and solidification before reaching the substrates. These particles, known as fine particles, were deposited in between and along with the splats. The process was evident from the fine round particles as seen as in Fig. 1c and d.

The silver content in Al2O3/Ag coatings was quantified by ICP-OES and shown in Table 3. It could be seen that the silver amount in coatings was less than that in original powers, which resulted from the different volatility in the plasma torch at high temperature.

Fig. 2 showed the XRD patterns of plasma sprayed Al2O3 and Al2O3/Ag coatings. It can be seen that all the patterns showed peaks at \(2\theta = 25.80^\circ, 35.28^\circ, 37.94^\circ, 43.62^\circ, 52.75^\circ, 57.67^\circ, 66.89^\circ\) and \(68.36^\circ\), which corresponded to \((012), (104), (110), (113), (024), (116), (214)\) and \(300\) reflections of \(\alpha\)-Al2O3, respectively. The corresponding peaks were indexed according to PDF#10-0173. Besides, the diffraction patterns displayed some characteristic peaks of \(\gamma\)-Al2O3, which were attributed to the \((321), (400)\) and \((511)\) planes (PDF#10-0425). The as-sprayed Al2O3 and Al2O3/Ag coatings had a dominant phase of \(\alpha\)-Al2O3 with a small amount of \(\gamma\)-Al2O3 as shown in the Fig. 2.

In XRD patterns, the intensity of the silver peaks was in accordance with the concentration of silver in the coatings, as shown in Table 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Original powders (ppm)</th>
<th>Al2O3/Ag coatings (ppm)</th>
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<tbody>
<tr>
<td>A1</td>
<td>1</td>
<td>0.27</td>
</tr>
<tr>
<td>A2</td>
<td>10</td>
<td>3.18</td>
</tr>
<tr>
<td>A3</td>
<td>100</td>
<td>13.78</td>
</tr>
<tr>
<td>A4</td>
<td>1000</td>
<td>145.96</td>
</tr>
<tr>
<td>A5</td>
<td>10 000</td>
<td>4963.68</td>
</tr>
</tbody>
</table>
values around 77.44°, respectively. Titanium alloy substrate had a lower contact angle of silver nanoparticles in the coatings. There were many pores on the as-prepared coatings (Fig. 3). It was speculated that the high contact angle values could be due to the pores among the rough surface of the coatings. Some researchers reported the relationship between the presence of bacteria and contact angle, and suggested that the hydrophobic surface had ability in inhibiting bacterial adherence and could be beneficial for the antibacterial application.\(^{22}\)

Fig. 4 showed the results of the antibacterial test on the plasma sprayed Al\(_2\)O\(_3\) and Al\(_2\)O\(_3\)/Ag coatings. It can be seen that the percent reduction of \(E.\) coli and \(S.\) aureus cultured on A3–A5 was 100% after 48 h incubation, indicating the strong antibacterial activity. In contrast, no considerable antibacterial activity was observed on A0. The reduction in bacterial viability increased from A1 to A2 as the concentration of silver in coatings increased (Table 3). Significantly better antibacterial activity against \(S.\) aureus was observed on A1 and A2 than that against \(E.\) coli. The detailed reduction in bacterial viability of the as-prepared coatings against \(E.\) coli and \(S.\) aureus were shown in Table 4.

Fig. 5 and 6 showed the surface adherent of \(E.\) coli and \(S.\) aureus on the plasma sprayed Al\(_2\)O\(_3\) and Al\(_2\)O\(_3\)/Ag coatings. As was shown in Fig. 5g–n, no \(E.\) coli was observed to adhere on A3–A5, exhibiting the strong anti-adhesive property. In contrast, many rods-like \(E.\) coli was found on sample A0 of the pure Al\(_2\)O\(_3\) coating (Fig. 5a and b). A remarkable decrease in bacterial adhesion was observed from A0 to A2 (Fig. 5e and f), and \(E.\) coli were randomly distributed and formed colonies of only a few bacteria on A2 (Fig. 5e and f). Similar findings have also been found for the adhesion of \(S.\) aureus. No adhesion of \(S.\) aureus was observed on A2–A5 (Fig. 6e–n), and \(S.\) aureus could only be found on A0 and A1 (Fig. 6a–d). Many grape-like clusters of \(S.\) aureus were

<table>
<thead>
<tr>
<th>Sample</th>
<th>A0</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
<th>A5</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E.) coli</td>
<td>0%</td>
<td>43.1% ± 2.3</td>
<td>96.8% ± 3.7</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>(S.) aureus</td>
<td>0%</td>
<td>51.0% ± 1.7</td>
<td>99.6% ± 0.8</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>

Table 4 Reduction in bacterial viability (%) of \(E.\) coli and \(S.\) aureus cultured for 48 h on the as-prepared coatings
observed on sample A0 (Fig. 6a and b) and S. aureus was just a few scattered distributions on A1 (Fig. 6d). It was assumed that the anti-adhesive property of the coatings should be attributed to a combined effect of antibacterial property and hydrophobic surfaces of the Al₂O₃/Ag coatings.

Fig. 7 showed the amounts of the released silver ions from the Al₂O₃/Ag coatings as a function of the elapsing time in deionized water. It was used to demonstrate the silver release behavior and trend of the Al₂O₃/Ag coating in the macroscopically environment. The amount of released silver from A2 to A5 increased obviously with the increasing of the content of AgNPs in the coatings. An initial burst release from the coatings was observed, and then the release rate slowed down gradually. Silver ion could be released from the Al₂O₃/Ag coatings, which was thought to be determinant on the excellent antibacterial properties of A2–A5.

4. Discussion

Silver has been extensively studied as an additive to endow ceramic coatings with antibacterial activity. Liu et al. reported a
negative and Gram-positive bacteria. Surface coatings had good antibacterial activity against Gram-negative and Gram-positive bacteria. It has been also reported that silver nanoparticles can inhibit the growth of bacteria. Several studies have shown that silver nanoparticles have high antibacterial activity against both Gram-negative and Gram-positive bacteria.

The antibacterial ceramic coatings contained Ag with concentration from 1.0 to 5 wt%. In this study, the plasma sprayed Al2O3/Ag coatings with silver nanoparticles as low as 10 ppm had strong antibacterial activity against E. coli and S. aureus. It was assumed that the enhanced inactivation of bacteria should be attributed to a combined effect of Ag nanoparticles and the hydrophobic surfaces of the Al2O3/Ag coatings.

Silver nanoparticles had high chemical activity and nanometer sized surface features which enhanced bactericidal capability. It has been also reported that silver nanoparticles demonstrated excellent antibacterial activity when compared with the other available silver antibacterial agents. The addition of silver nanoparticles with a size of 60–120 nm significantly enhanced the bactericidal effect of Al2O3/Ag coatings. The Ag nanoparticles or Ag+ attached to the cell membrane and also penetrated inside the bacteria. These species preferably interacted with the sulfur-containing proteins in the cell as well as with phosphorus-containing compounds such as DNA, finally leading to the death of bacteria.

The hydrophobicity of Al2O3/Ag coatings was another important factor influencing their antibacterial properties. It was known that most of infections were caused by the adhesion and colonization of bacteria on the surface. Once adhering to material surface, bacteria tended to form a biofilm by producing a matrix of largely extracellular polysaccharides. The biofilm would make the bacteria highly resistant to antibacterial agents, thereby leading to persistent and chronic infections. One of the most effective methods to improve the antibacterial efficacy was to avoid or reduce the initial adhesion of bacteria to surfaces. In order to ameliorate these problems, much more attention has been focused recently on hydrophobic and superhydrophobic surface treatment technologies and their repellent antibacterial effects. Some researchers have demonstrated that the hydrophobic surface had ability in inhibiting bacterial adherence. In turn, antibacterial surface could inhibit the adhesion and colonization of bacteria. The hydrophobic surfaces of A2–A5 had excellent anti-adhesive property toward both E. coli and S. aureus, which were in good agreement with these findings. The Al2O3/Ag coatings with hydrophobic surfaces reduced the initial adhesion of bacteria and prevented biofilm formation, thus improving the response of bacteria to antibacterial agents, which was beneficial to perform the antibacterial function.

The concentrations of silver played an important role in antibacterial activity, cytotoxicity, corrosive and the tribological properties. It was generally accepted that the antibacterial ability increased with increasing silver concentrations. But high doses of AgNPs could induce cytotoxicity leading to safety concerns. Song et al. showed that the silver-containing calcium phosphate coatings at high silver concentrations exhibited cytotoxicity. There was also evidence suggesting that high concentration of AgNPs in the ceramic coatings had disadvantageous effect on their corrosive and the tribological properties. In this study, Al2O3/Ag coatings were optimized to use minimum amount of silver nanoparticles as low as 10 ppm and performed excellent antibacterial property. The low concentration of AgNPs could minimize the potential cytotoxicity of silver as well as reducing costs. Besides, plasma spraying had been widely applied to fabricate a variety of antibacterial ceramic coatings. Consequently, the low cost, the relative simplicity of manufacturing procedure, and effective antibacterial properties, made it reasonable to anticipate the greater applications of the Al2O3/Ag coatings in microbiologically influenced corrosion, water treatment industry and environmental protection etc.

The antibacterial mechanism of Al2O3/Ag coatings was discussed on basis of Gouy-Chapman diffusion theory and Stern model as auxiliary theory for traditional antibacterial mechanism. When Al2O3/Ag coatings were in contact with the solution, silver would be ionized to silver ions and the surface of sample would be negatively charged. The interface between the Al2O3/Ag coatings and liquid phase was an electrical double layer.

![Fig. 7](image-url) Concentrations of silver released from the alumina–nanosilver coatings in deionized water as a function of time.

![Fig. 8](image-url) Illustration of silver ion released from the alumina/silver coatings in deionized water.
which consisted of Stern layer tightly adsorbed on the interface and the diffusion layer extending to the bulk solution as shown in Fig. 8. The silver ions concentration increased from bulk solution to the charged surface of coatings. It was assumed that there were two kinds of situations: silver ions in solution played a vital role in the antibacterial process when $C_{Ag^+}$ (silver ions concentration in bulk solution, denoted as $C_{Ag^+}$) was high enough; if not, the silver ions on the surface killed bacteria via a direct contact-killing action. We roughly speculated that the contact-killing action was the main way to destroy microbes for A1–A5.

5. Conclusions

In our work, antibacterial alumina coatings with five kinds of different amounts of AgNPs have been deposited on titanium alloys substrates by plasma spray. Feedstock powders were prepared by mixing $\alpha$-Al$_2$O$_3$ powders with 1 ppm, 10 ppm, 100 ppm, 1000 ppm and 10 000 ppm AgNPs. The results showed Al$_2$O$_3$/Ag coatings with more than 10 ppm silver nanoparticles exhibited good anti-adhesive property and antibacterial activity against E. coli and S. aureus, which made them suitable for applications in microbiologically influenced corrosion, water treatment industry and environmental protection etc.

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Notes and references


