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Development and characterisation of novel anti-bacterial S-phase based coatings

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ABSTRACT

It is well-known that biologically active Ag/Cu ions are strong bactericides and silver or copper nanoparticles have been used in polymer-based antibacterial coatings. However, their poor durability has limited their use in tribological applications. This problem has been largely addressed recently by developing novel plasma co-alloying of austenitic stainless steel surfaces with both nitrogen and Ag/Cu to form wear resistant antibacterial S-phase. However, this technology is only applicable to austenitic stainless steel as the S-phase cannot be formed to other materials.

In this study, S-phase based anti-bacterial coatings have been, for the first time, developed using magnetron sputtering through co-deposition of austenitic stainless steel with Ag/Cu to form hard S-phase doped with Ag, Cu or both in monolayer and multilayer structures. These coatings were fully characterised using multiple techniques such as SEM, TEM, XRD, GDOES and anti-bacterial tests. It has been found that it is possible to produce dense Ag and Cu doped S-phase layer with significant anti-bacterial efficacy. This was achieved while preserving the advantageous properties of the S-phase microstructure. As opposed to the popular diffusion based S-phase production such as plasma nitriding, this technology can also be applied on all kinds of surfaces, including low-cost steel surfaces, polymers and ceramics.

1. Introduction

Hospital Acquired Infections (HAI) increase the mortality rate and cause an increased demand for intensive care units, extended post-operation hospital stays and additional surgical intervention [1]. Nosocomial infections claim the life of 80,000 people annually in the United States of America (USA) making it the eighth highest cause of loss of life in the USA [2]. This also brings about a cost of more than $5 billion annually [2]. In the European Union Surgical Site Infections (SSI) are among the most common form of HAIs [3].

Medical devices such as surgical implants have brought about improvement in the quality of life of those who require them. However, the hospital stay and implantation of such devices can cause the proliferation of bacteria such as gram-positive *Staphylococcus aureus*. This occurs due to bacterial adhesion to equipment utilised during surgical intervention such as scalpels, scissors and the surgical implants themselves [4]. Other surfaces found within the hospital such as door knobs, bed side tables can also harbour infectious organisms which often spread quickly through people's hands [5]. Prophylactic measures through antibiotic administration or implementation of strict hygiene procedures are known to reduce or limit the negative impact of such bacteria but not prevent it completely [4,6]. Around 5% of primary Total Hip Joint Replacement (THJR) surgical sites become infected while there is a probability of 15%–20% that the revision surgery is also infected [4,6]. Complex infections often require revision surgery as antibiotic treatment is often unable to control the localised infection [6]. Over-reliance on antibiotics causes high predominance of outbreaks of antibiotic resistant bacteria such as *Methicillin-resistant Staphylococcus aureus* which are not unheard of in hospitals [7].

Implantable devices including bone plates, external fixation devices, nails and screws are often manufactured from austenitic stainless steel (AISI 316L alloy) owing to its attractive properties (cost, good corrosion resistance and biocompatibility) [8]. Such an alloy however suffers from significant pitting and crevice *in vivo* corrosion, excessive wear (including fretting wear), local bacterial infection or a combination of such failure causes [8–13]. Such surface phenomena produce metallic debris in the immediate area while causing excessively high levels of dissolved metal ions (such as nickel which is a known allergen [14] and carcinogen [15]) in the body fluids and organs causing serious medical complications [15,16].

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High performing surgical grade metals such as titanium and cobalt-chromium are available; however they cost up to ten times more than austenitic stainless steel [15]. Alternatively, one can surface engineer austenitic stainless steel in order to enhance the surface mechanical properties such as corrosion and wear resistance. It has been proven that austenitic stainless steel can be surface engineered through a low temperature thermo-chemical surface diffusion treatment (temperature $< 430\,^{\circ}C$ in a nitrogen containing atmosphere) [13]. Such treatments create an *S-phase* layer at the surface which exhibits significantly improved mechanical properties. However, it is known that S-phase can be formed only on some specific metallic materials including austenitic stainless steel, Co-Cr alloys and Ni-Cr alloys [13].

S-phase surfaces can be also be produced through magnetron sputtering techniques where austenitic stainless steel is deposited onto substrates within a nitrogen containing atmosphere [17]. Such surfaces have shown to exhibit all the superior properties of diffusion S-phase layers albeit in a narrower layer (2 μm) [18–20]. Magnetron sputtering introduces advantageous flexibilities where one can co-deposit S-phase together with other alloying elements not traditionally associated with S-phase. The introduction of such elements is a feasible way to elicit novel properties within S-phase coatings albeit no reports of such studies are available at the time of writing. S-phase diffusion layers on the other hand have been previously alloyed with silver or copper [21,22]. Silver and copper have received significant attention in surface research targeting the medical industry owning to their high efficiency with which they eliminate bacteria [23,24]. The aim of this study was to investigate and report for the first time the microstructural characteristics and anti-bacterial efficacy of S-phase coatings containing silver or copper in various monolayer and multilayer architectures.

2. Experimental details

2.1. Substrate materials

Annealed industrial grade AISI 316 (having a composition (wt%) of 17% Cr, 10.2% Ni, 2.5% Mo, 2% Mn, 1% Si, 0.08% C, 0.045% P, 0.03% S and Fe balance) was utilised during the preparation of the specimens. These specimens were prepared from a 14 mm round bar (cut at 1.2 mm thicknesses for anti-bacterial studies, supplier: RS components UK) and a 25.4 mm round bar (cut at 6.2 mm thicknesses for other characterisation analysis, supplier: RS components UK). All specimens were progressively ground to a finish level of 1200 grit size using SiC sand paper after which they were polished to a mirror finish using diamond suspension paste (1 μm). Specimens were thoroughly cleaned in warm acetone before loading in the deposition machine.

2.2. Coating deposition

2.2.1. Machinery setup

The coatings presented in this study were produced using a Closed Field Unbalanced Magnetron Sputtering Ion Plating Machine (CFUMSIP) UDP-350/4 which was manufactured by Teer Coatings Ltd. (UK). A plan view of the setup used to deposit the monolayer coatings in this study is presented in Fig. 1. Two AISI316L stainless steel targets with a chemical composition (wt%) of 16.6% Cr, 11.02% Ni, 2.02% Mo, 1.26% Mn, 0.43% Si, 0.024% C, 0.04%N, 0.032% P, 0.002% S with an Fe balance were utilised in this study. One chromium target (99.5% purity) was utilised for all coatings and a silver (99.95% purity) or copper (99.5% purity) was utilised in order to produce alloyed S-phase coatings.

2.2.2. Deposition procedure

Prior to coating production, the sputtering machine and targets were ion cleaned using a reproducible pre-programmed argon gas only run in order to avoid target nitrogen 'poisoning'. Coating deposition was started only after a base pressure of 10^{-6} Torr was attained with a vacuum diffusion pump so to minimize contamination. Testo temperature sensitive labels were used in order to confirm the maximum temperature during deposition. A piece of polished silicon wafer was loaded alongside the AISI 316 specimen in order to facilitate fracture analysis.

The basic parameters utilised to deposit all the coatings in this study were as follows: 900 s of pre-treatment ion cleaning using a bias voltage of -400 V and argon only plasma, 310 s of chromium interface layer deposition with a target current of 1A and a specimen pulsed bias voltage of -60 V (having a frequency of 250 Hz and a pulse width of 500 ns), deposition of S-phase mono/multilayer with a AISI 316L target current of 1.5A and a specimen pulsed bias voltage of -60 V (having a frequency of 250 Hz and a pulse width of 500 ns) and a nitrogen flow rate of 8 sccm. Additions of silver or copper were performed during this step as described in the subsequent sections. Argon flow is 8sccm throughout all the recipe. Such parameters were chosen after a parameter optimization study. The coated specimens were allowed to cool down under vacuum before extraction from deposition chamber. The maximum deposition temperature during the treatment was found to be $< 204\,^{\circ}C$.

2.2.2.1. Monolayer coatings. The homogeneous monolayer coatings were performed by simply powering the target of the antibacterial agent and the AISI316L simultaneously during the S-phase deposition step. The deposition time of this step was varied in order to produce an overall coating thickness of 2 μm. Three coatings for each antibacterial agent were performed using the following target current settings during the S-phase deposition step only and coating designation: silver 0.2A (SAglow), 0.35A (SAgmid), 0.5A (SAghi) and copper 0.32A (SCulow), 0.43A (SCumid), 0.54A (SCuhi). A high silver concentration S-phase monolayer coating was produced using similar techniques for microscopic analysis. All specimens were mounted on a jig with a target to specimen distance of between 63 mm to 73 mm and the specimen holder rotation was set to 5 rpm.

2.2.2.2. Multilayer coatings. These coatings consist of layers of equal thicknesses alternating between pure S-phase and silver/copper. The setup utilised for multilayer coatings was similar to that of Fig. 1 however only one AISI 316L target was employed which was mounted opposite that silver/copper target in order to form sharp interfaces between the layers. The target current settings utilised were 0.36A for silver and 0.51A for copper. Three coatings for each antibacterial agent with varying layer thicknesses were performed after depositing the chromium interface layer using the following layer thicknesses (thickness was controlled through specimen holder revolution speed): silver 2.5 nm (SAg2.5), 10 nm (SAg10), 35 nm (SAg35) and copper 2.5 nm (SCu2.5), 10 nm (SCu10), 35 nm (SCu35). Specimen holder rotation was set to 6.5 rpm, 1.5 rpm and 0.5 rpm in order to produce the 2.5 nm, 10 nm and 35 nm multilayer coatings respectively. Owning to the nature of copper and affinity to nitrogen the copper layers were deposited in an atmosphere that contained only argon while silver containing multilayers were deposited in argon and nitrogen containing atmosphere. A barrel-type sample holder with target to specimen distance of 73 mm was used for depositing multilayer coatings. A silver or copper layer was deposited as the final top layer with the respective thickness.

2.3. Microstructure characterisation

A JOEL 7000F (Japan) Scanning Electron Microscope (SEM) equipped with a calibrated Oxford Instrument (UK) Wave Dispersive Spectroscopy (WDS) detector was utilised and chemical composition analysis while the secondary electron detector was used for microscopic imaging of coating surfaces and fracture cross-sections. The SEM was operated at 20 kV and a 10 mm working distance for imaging and 10 kV for WDS investigations. Chemical depth profiling was performed using