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Antimicrobial brass coatings prepared on poly(ethylene terephthalate) textile by high power impulse magnetron sputtering

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ABSTRACT

The goal of this work is to prepare antimicrobial, corrosion-resistant and low-cost Cu65Zn35 brass film on poly(ethylene terephthalate) (PET) fabric by high-power impulse magnetron sputtering (HIPIMS), which is known to provide high-density plasma, so as to generate a strongly adherent film at a reduced substrate temperature.

The results reveal that the brass film grows in a layer-plus-island mode. Independent of their deposition time, the obtained films retain a Cu/Zn elemental composition ratio of 1.86 and exhibit primarily an α copper phase structure. Oxygen plasma pre-treatment for 1 min before coating can significantly increase film adhesion such that the brass-coated fabric of Grade 5 or Grade 4–5 can ultimately be obtained under dry and wet rubbing tests, respectively. However, a deposition time of 1 min suffices to provide effective antimicrobial properties for both *Staphylococcus aureus* and *Escherichia coli*. As a whole, the feasibility of using such advanced HIPIMS coating technique to develop durable antimicrobial textile was demonstrated.

1. Introduction

The surface properties of fabric materials are very important, as the applications of textiles depend strongly thereon. Numerous surface modification approaches have been considered for realizing specific surface properties. For example, surface metallization of the fabric produces electrical conductivity [1,2], which supports various functions for applications in the textile industry. These include electromagnetic shielding (EMS) [3], and antistatic [4] and antimicrobial [5,6] applications. The spread of drug-resistant bacteria (such as methicillin-resistant *Staphylococcus aureus*, MRSA) and the great increase in hospital-acquired infections have motivated the development and application of antimicrobial materials for preventive purposes, in preference to the conventional concept of disinfection. Possible applications for antimicrobial textile are surgical gloves, face mask, bed linen, etc.

Various approaches have therefore been developed to functionalize textile materials for antimicrobial purposes in recent years to reduce the risk of disease infection. These developments have involved in large part the bacteria-killing properties of silver and copper [7]. They include wet processes such as the electroless plating of antimicrobial metal [7,8], the sonochemical irradiation of nanoparticles [9,10], and the impregnation with organic/inorganic substances [11,12]. Several of these exploit wet chemical routes and some of these have inevitable shortcomings, such as the need for wastewater handling and unsatisfactory durability. Vacuum coating processes have been considered in recent years to satisfy all of the requirements of the antimicrobial treatment of textiles. Among such vacuum coating processes, magnetron sputtering has been utilized commercially to deposit antimicrobial metal [13,14]. This coating technique is well developed and its development is ongoing [15–17]. These efforts have been resulted great steps being made toward making textile treatment cleaner.

One emerging technique for magnetron sputtering involves the high-power impulse magnetron sputtering (HIPIMS) source: a high-voltage pulse is generated to provide high density plasma, finally to form a strongly adhered film at a reduced substrate temperature. Based on this unique power source, an antimicrobial treatment for textiles has been proposed in which silver is used as the raw material [18]. Silver and copper metals both inherit inorganic antimicrobial agents, which are environmentally friendly, safe and durable [19]. They are widely used, and have been proven to be effective in reducing infection [20,21]. However, despite its strong antimicrobial activity, silver metal has a limited range of uses because of its high cost. Copper metal, in contrast, has a low cost, but suffers from low corrosion resistance. It has been considered for use in Ti–Cu alloy coating by the HIPIMS technique [22]. Copper alloys, and Cu–Zn brass in particular, exhibit antibacterial character [23], corrosion resistance [24,25] and low material cost. In this study, they are deposited onto fabric. The microstructure of the deposited films was determined to elucidate the film growth behavior. The durability of the coated fabric was examined by performing standard rubbing and washing tests, respectively. The antimicrobial capacity of the coated fabric was also evaluated as a

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function of film thickness. Through this study, the main object of evaluating the feasibility of using such advanced HIPIMS coating technique to obtain durable antimicrobial textile can be achieved.

2. Material and methods

Poly(ethylene terephthalate), known as PET, in the form of a fabric of dimensions 29 cm × 19 cm was used as a substrate. It had a single filament diameter of 39 in., a density of 170 D and a weight of 273.4 g/m. Before it was coated with brass, RF oxygen plasma treatment was performed to remove surface contamination and to activate the surface of the fabric. The durability of the coated PET fabrics without oxygen plasma treatment was compared with that of those with such treatment. HIPIMS was carried out in a vacuum chamber in which was placed a single rectangular magnetron source with a target area of 11.4 cm × 34.5 cm (effective eroded area of 282 cm^2, from which power density was calculated). The HIPIMS power supply was manufactured by Taiwan Power Tech., and comprised a DC-1020A DC power unit and a SPIK 2000A-20 pulsing unit. The target current and voltage were measured using a Tektronix CT-4 high-current probe and a high-power voltage differential probe, respectively; the signals thus obtained were displayed and recorded using a Tektronix TDS 2022B digital oscilloscope.

3. Experimental

During deposition, the PET fabric was maintained 25 cm from a brass target (Cu65Zn35 wt.%, Cu/Zn elemental composition ratio of 1.86). The working pressure was fixed at a constant total pressure of 0.4 Pa. Table 1 presents the coating parameters. All of the deposition runs were operated without additional substrate heating. To ensure that the coating was performed in the HIPIMS mode, Fig. 1 plots the peak target current as a function of target voltage, which demonstrates that the peak target current, 140 A (equivalent peak target current density of 0.50 A/cm^2 and the corresponding peak power density of 3.23 kW/cm^2) was generated when a target voltage of 800 V was applied. This current fell into zone III in Fig. 1, which is the regular range for HIPIMS mode, as has been mentioned elsewhere [26,27]. The deposition time was varied to control the thickness of the film, to determine its microstructure, durability against rubbing and washing, and antibacterial efficacy.

The crystalline structure of the deposited films was identified using a Bruker D8SSS grazing incident angle X-ray diffractometer (GIXRD) with CuKα radiation at a grazing angle of 1°. A field-emission scanning electron microscope (FE-SEM, HITACHI S4800) was used to observe the surface morphology and cross-section of the deposited brass films. The elemental composition of the obtained brass films was determined using an energy dispersive spectrometer (EDS, HORIBA EMAX400) that was installed on the FE-SEM. The focused ion beam method (FIB, JEOL JIB-4601F) was used to reveal how the variation of the film thickness of the brass coating around the periphery of a single fiber.

Table 1
Overview of experimental parameters d for coating PET fabric with brass.

Oxygen plasma pre-treatment parameters	
RF power (W)	50
Working pressure (Pa)	13.3
Processing time (min)	1, 3, 5
Brass coating parameters	
Discharge voltage (V)	800
Peak current (A)	140
Average power (W)	8400
Peak power (kW)	912
Duty cycle, T_{on}/T_{total} (μs)	150/1000
Pulse frequency (Hz)	1000
Working pressure (Pa)	0.4
Deposition time (min)	1, 3, 5, 10

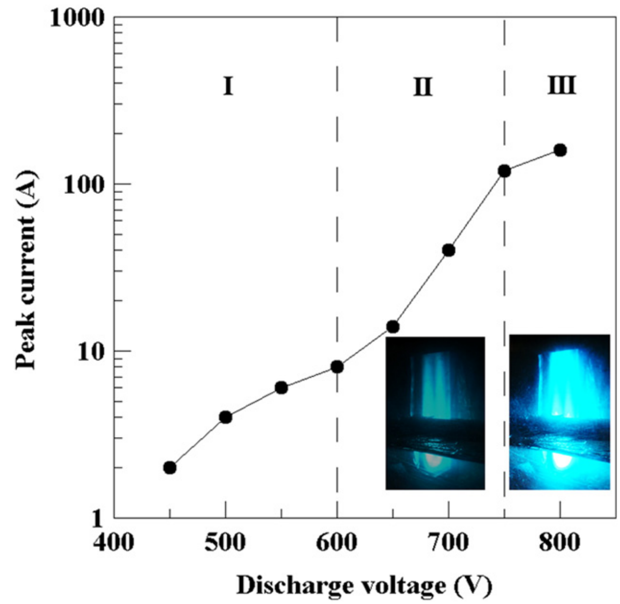

Fig. 1. Peak target current as a function of target voltage; insets show visible plasma discharge.

Two tests were utilized to evaluate the durability of the deposited brass coatings. The first was the color fastness during rubbing test (ISO 105-X12:2002, "Textiles — Tests for Colour Fastness — Part X12: Colour Fastness to Rubbing") [28] and the other was the color fastness to washing test (ISO 105-C02:1989, "Textiles — Tests for Colour Fastness — Part C02: Colour Fastness to Washing Test 2") [29]. For the first, the coated PET fabric as the specimen was rubbed against a standard cotton fabric for 100 cycles, and the extent of the transfer of the brass stain onto standard cotton fabric was evaluated using gray scales from Grade 1 (least color fastness, or the highest degree of transfer of the brass coating to the white cotton fabric) to Grade 5 (the highest color fastness). For wet rubbing, the standard cotton fabric was wetted with water and rubbed against the specimen as mentioned above. In the color fastness during washing test, each washing cycle involved mechanical agitation at 50 °C ± 2 °C for 30 min using a soap solution, followed by rinsing in water and drying at 60 °C ± 2 °C for 20 min. After 20 cycles of washing, the difference between the color of the brass-coated fabric and that of the as-coated fabric was evaluated using a Datacolor SF600X color meter. The color difference value is an index of the color fastness during washing.

The mechanical property test of the brass-coated fabrics concerns the change in mechanical properties that is caused by coating with brass. A vertical automatic test stand (ALGOL, JSV-H1000) with a digital push–pull gauge (ALGOL HF-100) was used to perform the tensile test to determine the ultimate load of the fabric. The test piece, clamped by the fixture, was a piece of the coated fabric with dimensions 10.0 cm × 1.5 cm. A strain gauge (KFP-2-120-C1-65L1M2R, Kyowa Electronic Instruments Co. Ltd., Tokyo, Japan) was attached to the surface of the test piece and connected to a data acquisition unit (DBU-120 A, Kyowa Electronic Instruments Co. Ltd.), which recorded elongation throughout the tensile test.

The antibacterial efficacy was qualitatively and quantitatively evaluated according to the JIS L 1902:2008, "Testing for antibacterial activity and efficacy on textile products" [30]. In the qualitative evaluation, *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) bacteria were the test inoculums. The test was performed aseptically to ensure the absence of any contamination. Each of the tests was carried out using an initial concentration of 1 ± 10^5 bacteria/ml. The inoculum was inoculated onto the raw PET fabric and the coated fabric of dimensions 28 mm × 28 mm. The pieces of fabricated fabric were hosted in sterilized Petri dishes at a temperature of 37 °C ± 1 °C for 18 h. Then,