Development of ‘smart’ metal-matrix or metal-dopant antimicrobial surface coatings by dry deposition techniques

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Abstract:
While bacterial and viral infections have existed for decades, the COVID-19 pandemic has raised awareness of the need to protect surfaces against germs and microbes. One solution is the use of antimicrobial coatings that offer a long-term solution, avoiding the use of chemical surfactants that are often not environmentally friendly. It also generally allows extending the life of the substrates. This work focuses on antimicrobial coatings based on copper and titanium nitride (TiN) deposited by atmospheric plasma spraying and evaporation (PVD), respectively and on a wide variety of substrates.

Keywords: antimicrobial coatings, Plasma Spray, Physical Vapor Deposition

1. Introduction

While bacterial, viral and fungal infections are not new to sciences, the COVID-19 pandemic was a reminder that living things can be exposed to new forms or mutations of pathogens. While healthcare facilities are the most likely environments for contamination, everyday equipment such as appliances, water faucets, doorknobs, public transportation seats and many other devices can also be prone to infection transmission.

Recently published research has focused on antimicrobial coatings for the food industry **[1-2]**, antimicrobial protection of medical implants **[3-6]**, dairy packaging **[7]** and protective masks **[8]**. When compatible with the substrate and the application, metallic coatings generally have good mechanical and aesthetic properties. Within the broad spectrum of metals, copper and silver have already demonstrated their effectiveness against bacteria and viruses, whether as surface coatings or as bulk materials **[9-11]**. Since the main reactions usually occur on the surface, it is somewhat unnecessary useless to operate with bulk metals. The development of copper- or silver-based coatings would not only allow us to take advantage of the surface activity at a lower cost but also reduce the potential metal toxicity effect by using smaller amounts.

In this work, we present two approaches for the development of antimicrobial coatings. The first approach consists in using a copper coating as matrix and titanium oxide (TiO_2) as antibacterial photocatalytic enhancer. The objective is to couple the bactericidal effect of copper to the photocatalytic activity of an available, low-cost and chemically inert compound such as TiO_2 **[12]**. The second approach uses copper and silver as dopants in a titanium nitride (TiN) matrix. TiN is very well known for its optimum wear resistance, biocompatibility, golden appearance and outstanding mechanical properties **[13]**.

Comparison of the ‘antimicrobial matrix’ and ‘antimicrobial dopant’ approaches could explain the nowadays mechanism of action on pathogens while the combination of materials could indicate the ‘synergistic’ or ‘additive’ impact on antiviral/antibacterial activity.

2. Experimental

Plasma Spray provides a good compromise between coating density/cohesion and porosity to maximize specific surface area and was used for the production of the copper-based coatings. The Cu:TiO_2 coating was deposited by coupling plasma spraying at atmospheric pressure (APS) of a copper powder (30-90 µm) and plasma spraying of a suspension (SPS) of submicron TiO_2 particles (20 wt%) in ethanol. This solvent is easily volatilized and burns during the process **[14]**. The plasma gas was argon and the net electric power of the plasma torch was 95 kW. The coatings (Cu and Cu:TiO_2) were produced by an APS/SPS system in the IRCER laboratory (**Figure 1**).

The coatings were deposited on 316L medical grade steel and thermoplastic (ABS). Antibacterial (*E-Coli*) tests were performed on the former coatings and antiviral tests (*SARS*

CoV-2) were performed in a P3 certified laboratory on the latter.

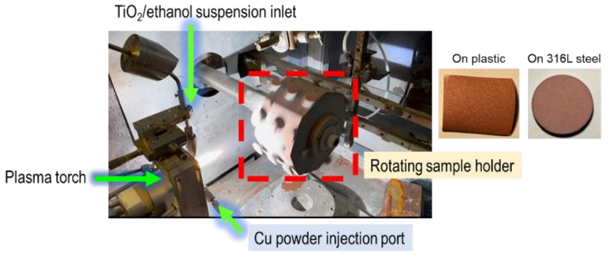

Figure 1: APS/SPS system for coating production at IRCER with examples of coatings on plastic and steel substrates.

Cathodic arc deposition (Arc-PVD) allows doping of the TiN matrix with antibacterial agents, such as Cu and Ag, at relatively lower temperatures and better doping control than plasma spray. It also allows the deposition of coatings on metal and plastic surfaces. In this study, the TiN-based PVD coatings were produced by Oerlikon Balzers™ (**Figure 2**). The TiN matrix is a BALIMED™ biocompatible layer obtained by Arc evaporation from a titanium target in a nitrogen atmosphere and the dopants are produced simultaneously by sputtering a target of silver or copper during the process.

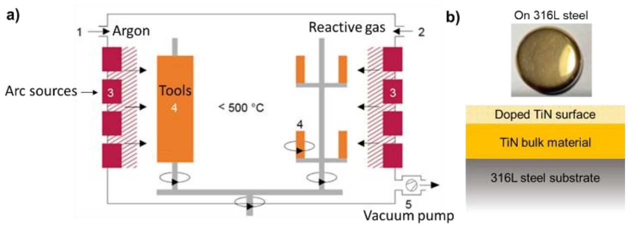

Figure 2: a) Schematic of the PVD system (from **[15]**) and b) example of doped TiN coating on 316L steel (photo) with its model below.

The morphology of all coatings was observed by a *LEO 1530VP™* field emission gun scanning electron microscopy (SEM-FEG) and the crystalline phases were identified by X-Ray diffraction on a Bragg Brentano θ/2θ *D8 ADVANCE* diffractometer with Cu Kα radiation from Bruker™. The surface composition of coating was obtained by X-ray photoelectron spectroscopy (XPS) from *Axis Ultra DLD Kratos™*. The surface roughness of plastic substrates was obtained with a *Keyence™* surface roughness meters. The contact angles on the surfaces, which is a quantitative measure of wetting of the coating by a liquid, was measured using a goniometer equipped by a *Pixelink™* camera.

The antibacterial activity of coatings against *Escherichia Coli* was measured according to *ISO 22196:2011*. The photocatalytic effect of TiO_2 was tested under pulsed UV light in a "LP box" from *Sanodev*. The system has a spectral range between 200 and 1200 nm and the irradiation dose was adjusted to 1.85 $J.cm^{-2}$. The antiviral efficiency against *SARS-CoV-2* was measured according to *ISO 21702:2019* in a P3-certified virology laboratory at the university hospital centre of Limoges. Finally, in order to estimate the metallic ion concentration released in the viral solution, ICP tests were performed on a *PerkinElmer Optima 8300™* optical emission spectrometer.

3.Results and Discussion

Surface roughness and wettability of coatings

The surface topography and the 3D numerical reconstruction of a copper coating are shown in **Figure 3**.

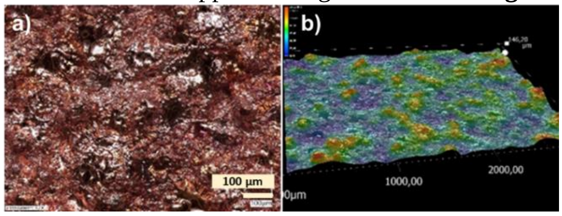

Figure 3: a) surface topography of the Cu coating on plastic substrate and b) corresponding 3D numerical reconstruction.

The average roughness (R_a) of the coating was 19 µm. The contact angle of water on the coating on plastic ABS was 86° and that of Diiodomethane was 40° (**Figure 4**).

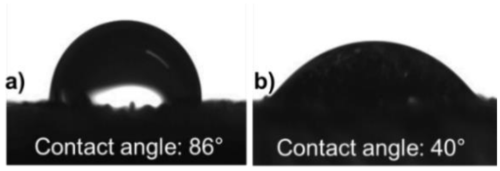

Figure 4: Contact angle of a) a polar solvent (water) and b) a disperser solvent (CH_2I_2) on Cu coating.

With both solvents, the copper-based coatings surface was hydrophilic (angle<90°). The calculated superficial tensions were 2.6±1.8 $mN.m^{-1}$ and 39.1±0.3 $mN.m^{-1}$ for the polar and disperser solvent, respectively. The total surface energy, which includes both dispersive (Wan der Waals) and polar (H-bonds) contributions ($\sigma_{Total} = \sigma_{dispersive} + \sigma_{polar}$) was about 47 $mN.m^{-1}$. This value is relatively high and indicates that the sample wettability by the microbial solution is quite good.

The average surface roughness of the PVD coatings (TiN:Ag and TiN:Cu) was 0.25 µm, a value well below that of the plasma sprayed coatings. Therefore, the microbial solution probably does not adhere on both coating types in the same way. The antiviral efficacy results of PVD on 316L steel and plasma-sprayed coating on an ABS plastic substrate are shown in **Figure 5**.

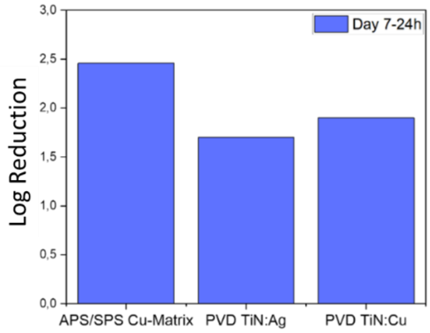

Figure 5: Anti-SARS-CoV-2 efficacy of the Cu-matrix and TiN-matrix surfaces.

Antiviral effectiveness of coatings

The Cu-based coating on ABS has an antiviral effectiveness over the decontamination threshold of 2 while the antiviral activity of the TiN based PVD coatings is lower even though they have already demonstrated a very high antibacterial efficiency, which led to the joint research project for antibacterial and antiviral coatings in the aerospace sector in 2020 **[16]**. At this point, we could not confirm that Cu matrix works better than the doped TiN matrix, because the coatings have a 'substrate memory' that is not the same in both cases.

In addition, the surface finish of PVD and plasma-sprayed coatings is not similar, which plays a critical role in the wettability of the sample. This point is the subject of our current study in which we try to compare the antimicrobial activity for coatings with the same surface condition.

Antiviral mechanism(s) of coatings

ICP results performed on the viral solution collected on the surface of the Cu-matrix revealed a remarkable increase of Cu ions more or less linear, from 3.78 $mg.L^{-1}$ directly upon exposure to 203.9 $mg.L^{-1}$ after 24h of contact with the virus (**Figure 6 (a)**).

In parallel, the XPS results showed that most of the copper on the surface is either metallic or bound to OH groups, probably from atmospheric contact (humidity). No Cu^{+} ions were detected on the surfaces (**Figure 6 (b)**). This means that the ions released in the viral solution are mainly Cu^{2+}, which act as antimicrobial agents. Such a hypothesis is currently under investigation to clearly define clearly the antiviral mechanism of copper on our coatings.

In addition, antiviral tests on PVD TiN-matrix coatings with a controlled surface roughness are planned to compare the 'antimicrobial matrix' to the 'antimicrobial dopant' approach.

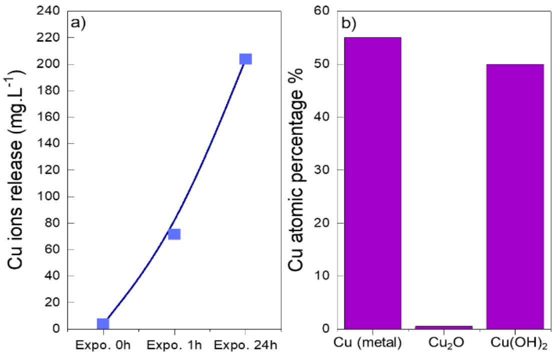

Figure 6: a) ICP results showing the Cu ions release in the viral solution from the Cu-matrix coating on ABS and b) the corresponding XPS on the coating surface.

Finally, since our development of antimicrobial surfaces is not exclusively aimed at antiviral efficacy, we have studied the possible combination of a bactericidal and photocatalytic effect on $Cu:TiO_2$ coatings. Despite the high temperature of plasma spraying, the presence of anatase, proven to be more active than rutile was confirmed by XRD but most of the TiO_2 is in rutile phase.

Three antibacterial (*E. Coli*) tests were performed on each sample and each test was repeated three times.

$Cu:TiO_2$ coatings, without pulsed light illumination, showed only a log reduction of 0.69±0.07 while after illumination, the log reduction exceeded the decontamination threshold, reaching 2.22±0.02.

Research is still in progress to understand the combined effect of bactericidal and photocatalytic effect. Further experiments on Cu alone and TiO_2 alone are to be performed. Also, cytometry experiments are underway to confirm the mechanism of pathogen destruction.

The results presented are those obtained on steel substrates, but within the framework of this project, a transfer to ABS plastic substrates is planned.

4.Acknowledgement

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