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Letters

Sars-CoV-2 (COVID-19) inactivation capability of copper-coated touch surface fabricated by cold-spray technology

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ABSTRACT

In this work, cold-spray technique was employed for rapid coating of copper on in-use steel parts. The primary intention was to alleviate the tendency of SARS-CoV-2 (COVID-19) virus to linger longer on touch surfaces that attract high-to-medium volume human contact, such as the push plates used in publicly accessed buildings and hospitals. The viricidal activity test revealed that 96% of the virus was inactivated within 2-hrs, which was substantially shorter than the time required for stainless steel to inactivate the virus to the same level. Moreover, it was found that the copper-coated samples significantly reduces the lifetime of COVID-19 virus to less than 5-hrs. The capability of the cold-spray technique to generate antiviral copper coating on the existing touch surface eliminates the need for replacing the entire touch surface application with copper material. Furthermore, with a short manufacturing time to produce coatings, the re-deployment of copper-coated parts can be accomplished in minutes, thereby resulting in significant cost savings. This work showcases the capability of cold-spray as a potential copper-coating solution for different in-use parts and components that can act as sources for the spread of the virus.

1. Introduction

SARS-CoV-2, commonly known as COVID-19 [1], is a pandemic spreading at a dreadful pace where close to 3 million infections have been reported globally [2]. Furthermore, neither medication nor vaccines are available at the time of this study; the only protection from this virus is by reducing the rate of its spread, especially by community transfer as these cases are difficult to track and trace. The transmission of COVID-19 virus between humans primarily occurs through respiratory droplets [3]. In one scenario, infective droplets can enter the respiratory system of a person when they are near (within one meter of) an infected person. Alternatively, the droplet transfer can occur indirectly, wherein the infective droplets latch onto the surface of an object and then gets transmitted to a healthy person touching the same object. While the prior scenario has been addressed by enforcing social distancing measures of at least 1.5 m [4,5], and in a more draconian approach through a lockdown, the latter scenario is potentially addressed by applying virus-inactivating solutions capable of rapidly reducing the lifespan of the COVID-19 virus.

In the last two decades, copper has been known for its antimicrobial property [6] and also proven to be capable of inactivating different types of viruses such as influenza A [7,8], Coronavirus 229E [9] and recently COVID-19 [1]. van Doremalen [1] reported that COVID-19 virus was more stable on stainless steel than on copper, where the virus was eradicated from the copper surface within 4-hrs. However, the source of their copper sample was unclear as they mentioned it as metal remnants. On the other hand, Victor et al. [8] reported the anti-virulent characteristic of cold-sprayed copper coating when exposed to Influenza A virus. To the best of the authors' knowledge, there is no study to investigate the behaviour of COVID-19 virus on cold-sprayed copper coatings, which is important as in-use components can be retrofitted with copper coatings and re-deployed in a very short period of time that can potentially slow down the spread of various viruses, including COVID-19.

Most existing high-to-medium human contact surface components are necessarily made of steel. Replacing all the existing steel surfaces by copper bulk parts is not a pragmatic option from both economical and practical aspects. To facilitate the use of existing parts, cold-spray technique can be employed to deposit copper coatings in quick time. In this process, high-pressure carrier gas (air, nitrogen or helium) propels metal particles at supersonic

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velocity onto a substrate. During collision, this kinetic energy provides sufficient energy for the metal particles to undergo severe plastic deformation and mechanically interlock with each other, thereby producing a thin dense deposit [10,11]. In this study, push plates are used as test coupons to assess the feasibility of copper coating via cold-spray technique. A push plate is a thin metal (2 mm) mounted on doors and functions as a site for a person to push and open a door when a door handle is not available. Similar to the door handles, push plates are operated by human contact. Consequently, push plates are exposed to chemical and biological contaminants, including bacterias and viruses. Moreover, in publicly accessed buildings and hospitals, such exposure is prominent and can become a source of disease transmission, especially when using stainless steel that does not exhibit adequate antibacterial and antiviral property [1,7,9].

In this work the authors have deposited copper coatings onto the stainless steel push-plates in a matter of 7 mins only, which is a marvellous demonstration of the application of the cold spray coating process for ongoing and future challenges arising from the pandemic. Moreover, this also translates to significant cost savings wherein the existing parts are not completely replaced but coated with copper in quick time and put back in service.

2. Experimental procedure

2.1. Cold spray

Copper coatings were deposited on a stainless-steel push plate[1] of dimensions 300 mm × 75 mm × 2 mm (Fig. 1(a)), typically installed on doors in commercial buildings in Melbourne, Australia. Locally-sourced copper powders (99.90 wt% Cu) with particle size ranging between 5 and 60 μm were used. In this study, a novel cold spray system (Lightspee3D) was employed. This system utilizes a stationary nozzle that injects metal powder vertically onto a moving substrate. The motion of the substrate is dictated by the six-axis robot arm controlled by a built-in algorithm capable of manufacturing complex geometry components. In conjunction with a nozzle exit temperature of 500 °C, air pressure of 3 MPa, a standoff distance of 16 mm, copper powder deposition was performed at a 45° angle onto the stainless steel push plate substrate. Two push plates were coated where one was tested in the as-deposited condition (3D Copper (N)), whereas the other was subjected to annealing post-heat treatment prior to testing (3D Copper Annealed (A)). Before the viricidal activity tests, the copper-coated plates were polished using an electric motor-driven steel brush to maintain a consistent surface finish across the copper coatings.

2.2. Material characterization

A Taylor Hobson Profilometer 7.1 was used to measure the surface roughness (Ra) of the stainless steel push plate and the copper coating at five different locations. The thickness and porosity in the copper coating were observed using an Olympus BX-61 optical microscope with proprietary image processing software. An average of five values along different cross-sections of the coating is reported.

2.3. SARS-CoV-2 viricidal activity test

The virucidal activity of copper was determined *in vitro* by exposure of the virus to copper. A virucidal agent inactivates the virus and would be expected to cause an irreversible, measurable reduction in the titre of the infectious virus compared to the virus only positive infection control. Sodium acetate was used as it is a known virucidal agent that causes irreversible reductions in viral titre.

A 50 μL volume of SARS-CoV-2 containing $10^{5.5}$ $TCID_{50}$ /mL ($TCID_{50}$ is a measurement of virus titre and represents the amount of virus that produces an infection in 50% of the cells exposed) was placed on small squares of copper, activated copper or stainless steel and left in contact for 1, 10, 30, 120 or 300 min at room temperature in a 24 well tissue culture plate. For the virus only positive infection control, a 50 μL volume of SARS-CoV-2 was added to an empty metal-free well. After the allocated time, 300 μL of assay media was added to the metal squares or virus only containing well to "wash" remaining virus off. The resulting media wash was quantified by $TCID_{50}$ assay, by the addition of 100 μL of wash to each of three replicate wells in a 96 well cell culture plate containing African Green Monkey Kidney Cells (Vero) pre-seeded overnight at $2x10^4$ cells/well. Virus containing wash was serially diluted three-fold across the plate for a total of nine different virus concentrations. Six of the wells contained assay media alone (i.e. no virus) and served as controls. Plates were incubated for three days at 37 °C in a humidified 5% CO_2 atmosphere, and virus-induced CPE scored visually with wells containing visible CPE scored as positive, and wells displaying no viral CPE scored as negative. The highest dilution at which 50% of wells were infected/scored positive with the virus (viral $TCID_{50}$) was determined using the method of Reed-Muench [12]. The virucidal effect was quantified as the log reduction in virus titre compared to the SARS-CoV-2 only positive infection control media titre. The SARS-CoV-2 only positive infection control defines the maximal viral titre that can be observed when the virus is not exposed to the viricidal agent of interest.

3. Results and discussion

3.1. Cold-spray copper coatings

Stainless steel push plate (Fig. 1a) was cold-sprayed by copper particle resulting in a textured copper coating (Fig. 1b) with a thickness of around 0.7 mm, produced within 7 min of spraying time with a deposition efficiency of about 56%. The coating was very dense with a porosity level of 2.1 ± 0.5%. The coated push plate was then polished, reducing the effective coating thickness to about 0.45 mm (Fig. 1c). The surface roughness of the coated plate after polishing was found to be 5.65 ± 0.76 μm, significantly higher than that of the original stainless steel push plate substrates (0.5 9 ± 0.08 μm). Finally, Fig. 1d exhibits a copper-coated push plate redeployed onto a door. The total time from spraying until push plate re-deployment was around 15–17 min. This has been achieved significantly in a short time period compared to replacing steel parts with new bulk copper push plates.

3.2. SARS-CoV-2 viricidal activity

Table 1 and Fig. 2 presents the viricidal activity results of SARS-CoV-2 virus when exposed to three different metallic surfaces and compared with COVID-19 only and positive control solutions. From the results, it is evident that copper-coated test coupons demonstrate a substantial reduction in the titration values; in other words, the activation capability of the COVID-19 virus. After 2-hr incubation time, 96% of the virus was inactivated when exposed to the as-deposited (N) copper coating, whereas 92% virus inactivation was achieved on the annealed (A) copper coating. When the virus had a prolonged exposure of up to 5-hrs to these surfaces, an inactivation efficiency of 99.2% and 97.9% for the as-deposited

[1] Chemical composition: 71.54 wt% Fe, 18.16 wt% Cr, 8.21 wt% Ni, 1.07 wt% Mn, 0.48 wt% Si, less than0.08 wt% C

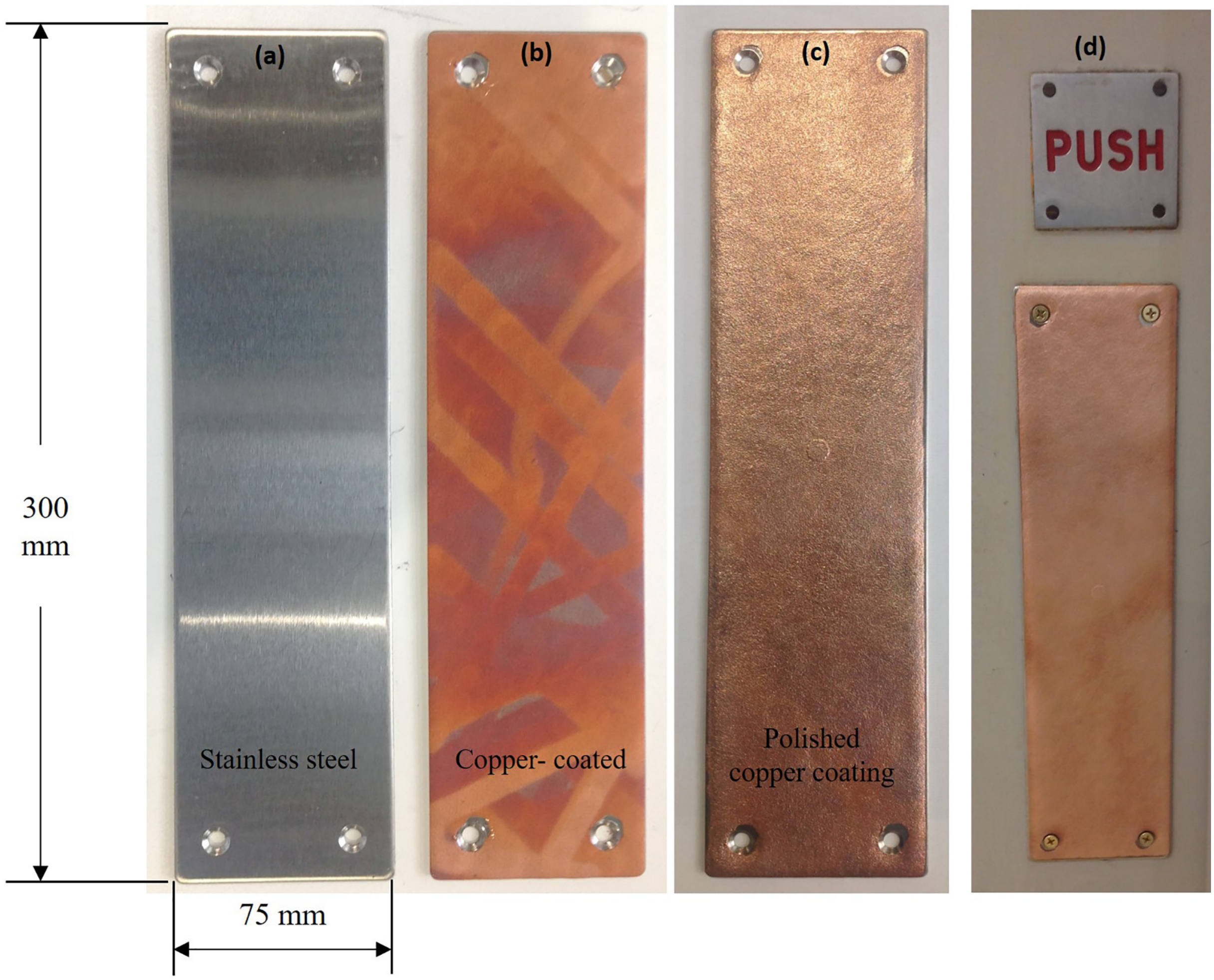

Fig. 1. Macro-photograph of (a) an in-use stainless steel push plate, (b) copper coating on stainless steel push plate, (c) polished copper coating; and (d) copper-coated push plate installed on a door.

Table 1
Evaluation of virus titres with respect to the exposure time.

	Length of incubation											
	1 min		10 min		30 min		120 min			300 min		
	Log Titre	Log Difference	Log Titre	Log Difference	Log Titre	Log Difference	Log Titre	Log Difference	% Reduction	Log Titre	Log Difference	% Reduction
3D Copper Annealed (A)	$10^{5.1}$	−0.4	$10^{5.0}$	−0.2	$10^{5.1}$	−0.4	$10^{3.9}$	−1.3	92	$10^{3.3}$	−1.9	97.9
3D Copper (N)	$10^{4.9}$	−0.5	$10^{5.1}$	−0.1	$10^{5.1}$	−0.4	$10^{3.4}$	−1.8	96	$10^{3.0}$	−2.2	99.2
Stainless steel	$10^{5.1}$	−0.4	$10^{5.2}$	0	$10^{5.1}$	−0.4	$10^{4.9}$	−0.3	49	$10^{5.5}$	0.3	0
Positive control	$10^{5.1}$	−0.5	$10^{5.0}$	−0.1	$10^{5.0}$	−0.5	$10^{4.6}$	−0.6	74.9	$10^{4.2}$	−1.0	90
SARS-CoV-2 only	$10^{5.6}$		$10^{5.6}$		$10^{5.5}$		$10^{5.2}$			$10^{5.2}$		

(N) and annealed (A) copper coatings, respectively. A similar observation was made by van Doremalen et al. [1], and they reported that no viable SARS-CoV-2 was found on copper after 4-hrs as opposed to stainless steel surface where the virus was detected up to 72-hrs of incubation. However, they used metal remnants as sources for surface exposure which could potentially differ from commercial metals present in high-medium volume contact surfaces. In this study, push plate test coupons were used, which characteristically represents steel parts exposed to high-medium human contact traffic. Additionally, using the advanced coating capability, it is shown in this study that a "quick and easy fix" to existing steel parts and in-use components can be carried out with coating copper in a very short time to mitigate the spread of COVID-19 virus.

Till-date, two possible theories have emerged to explain the anti-microbial property of copper surfaces. Firstly, copper in native form, Cu(I) and Cu(II) influences the antiviral property. A study by Warnes and Keevil [13] demonstrated that Cu(I) was the primary effector of norovirus inactivation. In a later study, Warnes et al. [14] further demonstrated that copper alloy with higher copper content (79–89%) inactivated noroviruses more rapidly than that of alloy with lower copper content (70%). Secondly, copper in a

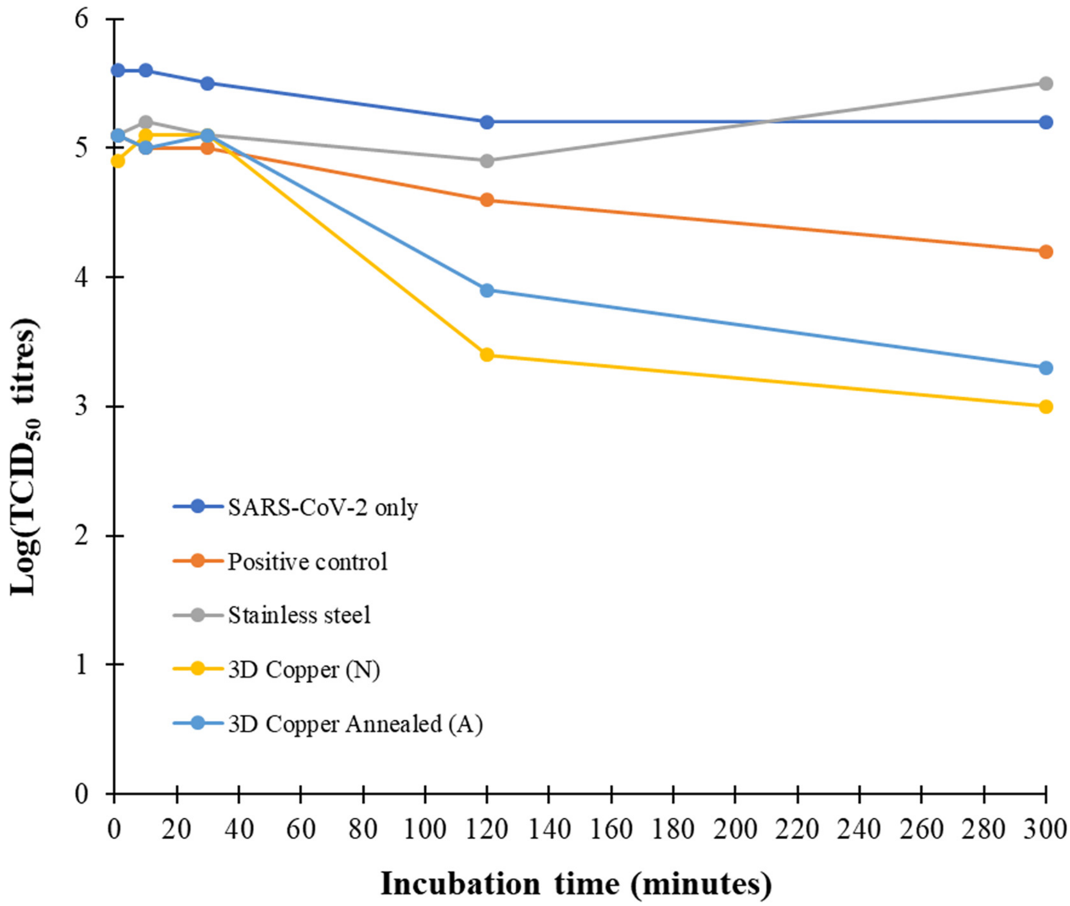

Fig. 2. Viricidal effect of 3D-printed Copper-coated and stainless steel metallic surfaces.

nano-scale form (nano-particle) exhibited virus-killing capability. A study by Fujimori et al. [15] demonstrated copper nano-particle with a size of 160 nm manifested anti-influenza A virus. These two mechanisms in part may have contributed to the anti-COVID19 property of the cold-sprayed copper coatings. Although the mechanisms of inactivation of viruses on copper surfaces are well reported, understanding the underlying mechanisms of COVID-19 virus inactivation on 3D-printed copper coating is a subject for further investigation [8,16].

4. Conclusions

This work highlights the application of cold-spray process to fabricate copper coatings onto in-use steel push plates in about 7 mins, with total time for re-deployment within 17 mins. Furthermore, the copper-coated test coupons were found to have substantially higher SARS-CoV-2 (COVID-19) inactivation characteristic compared to stainless steel, i.e. the inactivation efficiency was 96% and 99.2% for the as-deposited copper coating after a 2-hr and 5-hr incubation time, respectively. This test demonstrates the capability of cold spray technology to manufacture copper coatings with virus-killing property in a short time, thereby, making it possible to re-deploy coated parts back into service.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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