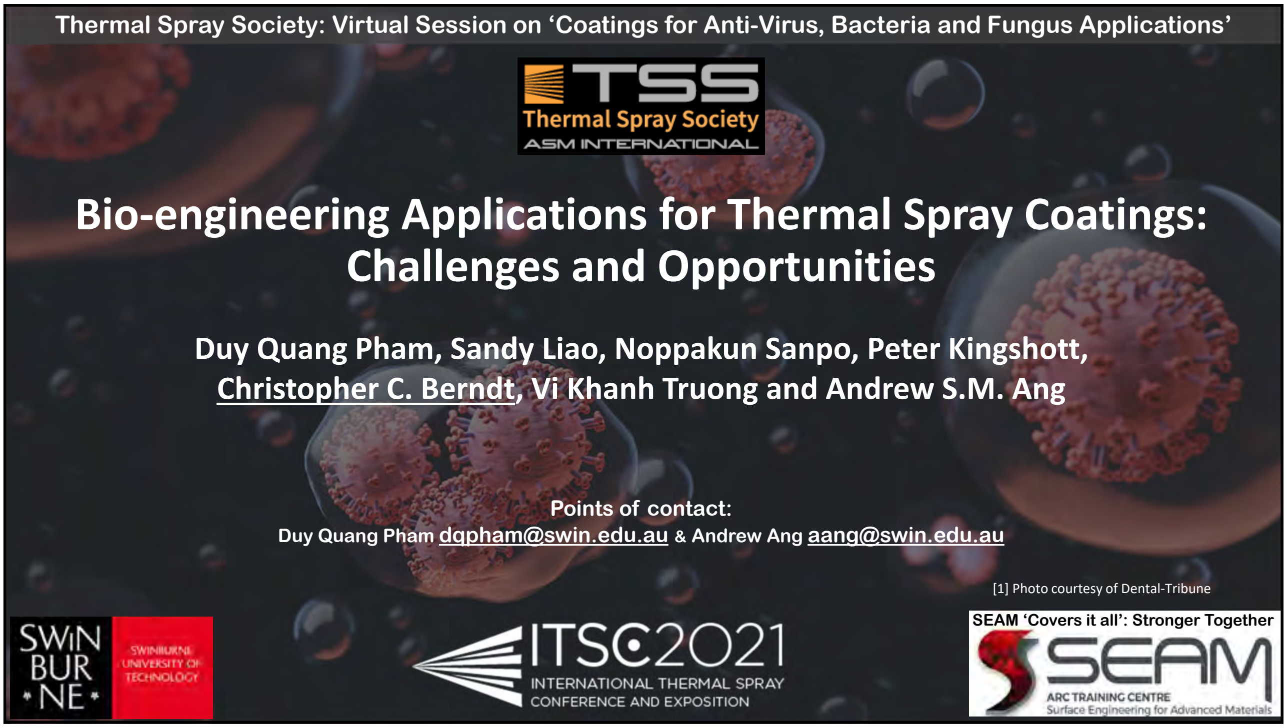

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DEDICATION and ACKNOWLEDGEMENT

Heath Care Staff and Essential Service Personnel have demonstrated their commitment and self-sacrifice.

They are working at the front line of the 2020 global pandemic during a crucial time of need.

Their devotion and dedication is inspirational.

We are all stronger when we work together.

THANK YOU

[2] Image courtesy of GoGraph 2 /11

2

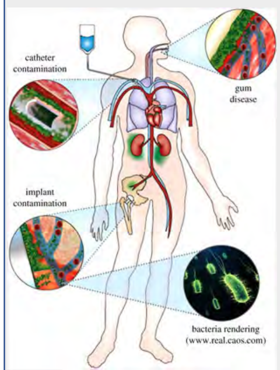
D.Q. Pham, S. Liao, N. Sanpo, P. Kingshott, Christopher C. Berndt, V.K. Truong and A.S.M. Ang

18 June 2020

Biofilms & Biofoulings Impact People & Society

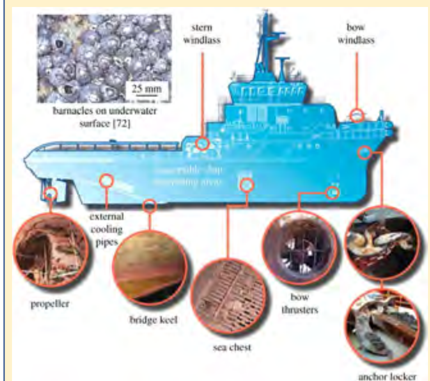
Field	Equipment/devices	Challenges
Medical	Orthopedic implants	Removal due to infection
	Respirators	Ventilator-associated pneumonia
	Contact lens	Eye infections
	Catheters	Urinary tract infections
	Haemodialysis	Infectious break-outs
	Dental implants	Periodontal disease, gingivitis
	Biosensors	Failure from fibrous encapsulation
Marine	Ship hulls	↑ fuel consumption
	Ship engines	↑ stress from extra drag
	Marine platforms	↑ structure stress/fatigue
	Metals	↑ biocorrosion
Industrial	Membranes	↓ flux
	Heat exchangers	↓ convection efficiency
	Fluid flow	Frictional loss in pipes
	Drinking water	Pathogens in potable water
	Fuels	Diesel fuel contamination
	Food, paper & paints	Food spoilage & health risks
	Metal-cutting fluids	Filter blockage & health risks

Physiological outcomes of infectious biofilms



Impacts:
- Health
- Quality of life
- Life style

Marine platform areas affected by biofouling



Impacts:
- Efficiencies
- Productivity
- Economics

Summary #1
- Biofilms & biofouling influence every aspect of society.
- The key: Understanding the science of surface engineering.
- The quest: Technological control of biofilms and biofouling.

[3] Bixler, G. D. et al. (2012)

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3

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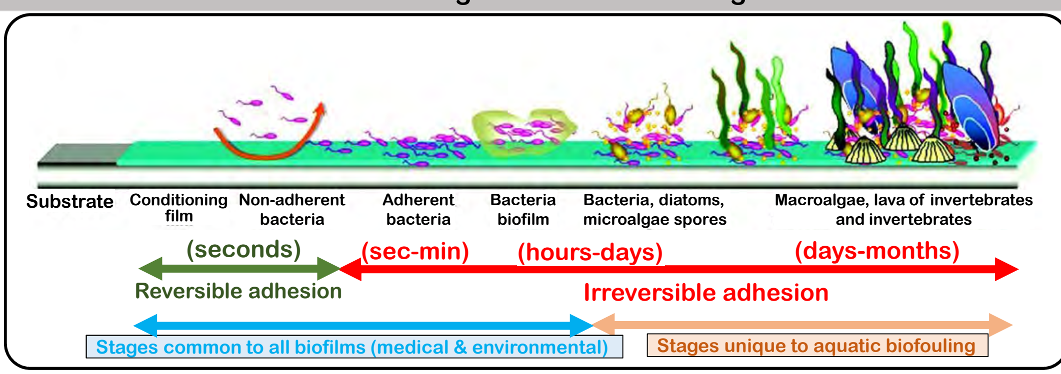
Defining Biofilms & Biofouling



Biofilm (medical and environment)
- Structured community of bacteria that attach and grow onto the surface of materials
- Bacterial biofilms are responsible for medical infections and environment problems.

Biofouling (aquatic biofouling)
- Anchored multicellular species, micro-algae, debris, marine invertebrates (barnacles, mussels, macroalgae).
- Affects piping & cooling towers; power plants and components exposed to water.

Summary #2
Biofilms & biofouling are a continuum of biological growths that are differentiated by time and propensity in size.

[4] Grzegorczyk, M. et al. (2018)

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D.Q. Pham, S. Liao, N. Sanpo, P. Kingshott, Christopher C. Berndt, V.K. Truong and A.S.M. Ang

18 June 2020

'High Velocity Oxygen Fuel' Carbide-Based Coatings: Marine Biofouling

Feedstocks

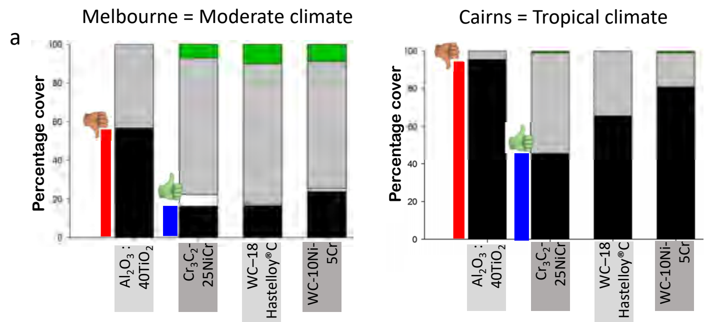
Atmospheric plasma spray (APS)
- Al_2O_3 : $40TiO_2$

High velocity oxygen fuel (HVOF)
- Cr_3C_2-25NiCr
- WC–18 Hastelloy®C
- WC-10Ni-5Cr

Surface Roughness (Ra, µm)

- Al_2O_3 : $40TiO_2$ samples = 0.26 µm
- Cr_3C_2-25NiCr = 0.10 µm
- WC–18 HastelloyC = 0.08µm
- WC-10Ni-5Cr = 0.08µm

Macrofouling



Biofouling
Bare surface
Slime / biofilm
Corrosion

Al_2O_3 : $40TiO_2$ → higher fouling relative to HVOF.

Summary #3
- Surface roughness can be controlled.
- Surface roughness influences biofouling.
- Coating chemistry influences biofouling.
- Successful new coating resists biofouling.

DMTC

[5] Piola, R. et al. (2018) 5 /11

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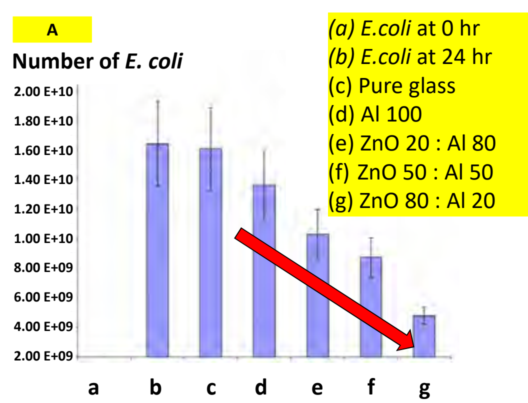
Cold Sprayed Coatings against *E. coli* Bacteria

A. ZnO : Al Coatings on glass slides: The antibacterial activity ↑ with ZnO concentration.

B. ZnO : Titanium Coatings on Al 6061: The antibacterial activity ↑ with ZnO content.

C. Hydroxyapatite-Ag : PEEK Coatings on glass slides: The antibacterial activity ↑ with HA-Ag nanopowder.

D. Chitosan-Cu : Al Coatings on glass slides: The antibacterial activity ↑ with CS-Cu content.



Summary #4
- Success for forming: (i) 'metal + ceramic' & (ii) 'metal + ceramic + polymer' composite.
- Demonstration of surfaces that are antibacterial.
- Antibacterial character ↑ with functional additive.

[6] Sanpo, N. et al. (2008) [7] Sanpo, N. et al. (2010)
[8] Sanpo, N. et al. (2009a) [9] Sanpo, N. et al. (2009b)

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6

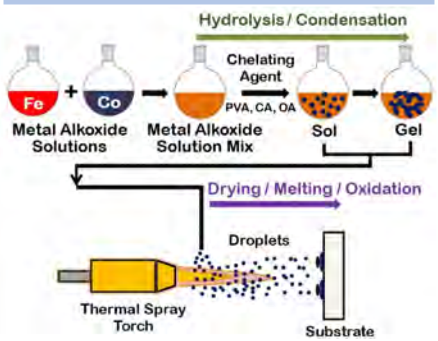
D.Q. Pham, S. Liao, N. Sanpo, P. Kingshott, Christopher C. Berndt, V.K. Truong and A.S.M. Ang

18 June 2020

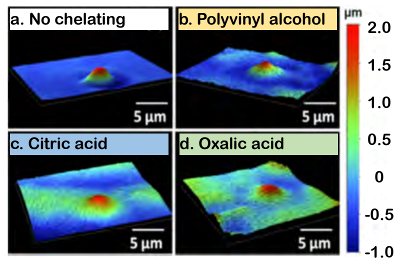
Solution thermal spray of Cobalt Ferrite: Bacterial response

Cobalt ferrite ($CoFe_2O_4$) either as nanoparticles, solutions or gels.
Prepared with polyvinyl alcohol (PVA), citric acid (CA) and oxalic acid (OA) as chelating agents.

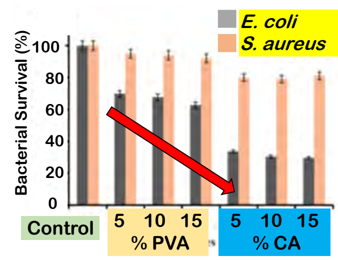
Solution thermal spray to deposit cobalt ferrite on polished mild steel.



Coating microstructure and topography is distinctive wrt feedstocks.



Effective antibacterial activity against *E. coli* and *S. aureus*.



Splat properties controlled by chelating agents.

Splat properties controlled by chelating agents.

- CA is more effective over PVA.
- *E. coli* is more influenced than *S. aureus.*

Summary #5
Opportunity: Coatings / films designed for focused functionality.

[10] Sanpo, N. et al. (2013a)

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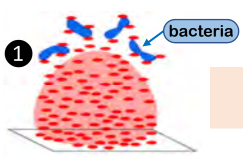
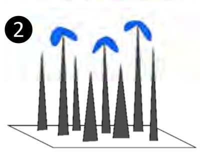
Strategies for Antibacterial and Antibiofouling Coatings

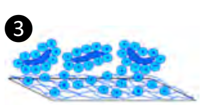
Antibacterial Coating Approaches



1. Biocide Releasing
Release of antibacterial agents to kill bacteria.



2. Contact Killing
Damage bacterial cell membrane with sharp nanostructured material.

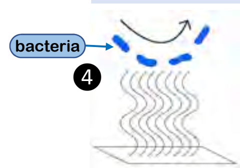


3. Immobilizing Cations
Release of antibacterial agents to kill adhered and adjacent planktonic bacteria.

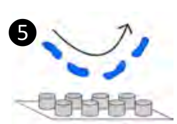
Summary #6
- Chemical and mechanical strategies to kill bacteria.
- Surface science and engineering knowledge is essential.
- Q. What is the role of thermal spray science?

Note: Common antibacterial agents are Ag, Cu, Zn, Ga, Se

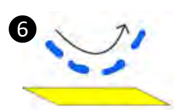
Antibiofouling Coating Approaches



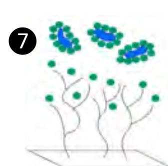
4. Steric Repulsion
Strong forces repel proteins.



5. Surface Topography
Surface curvature, pattern size and shape, and spacing to prevent micro-organism attachment.



6. Low Surface Energy
Prevent adsorption of micro-organism.



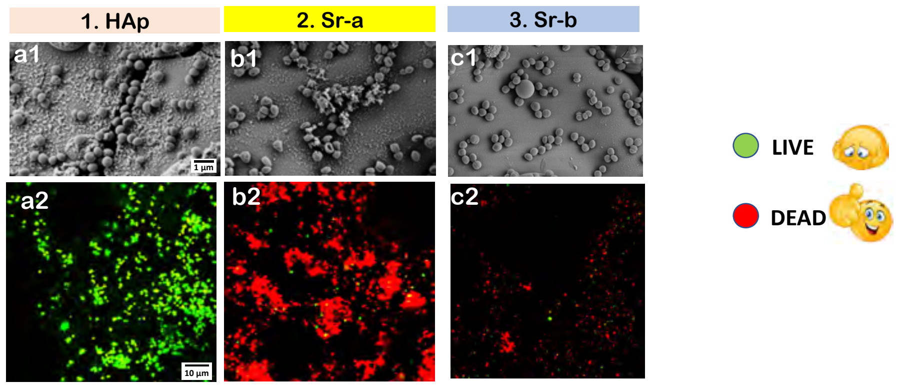
7. Electrostatic Repulsion
Cell disintegration by disrupting the negatively charged membrane of bacteria.

[11] Kurtz, I. S. et al. (2018)

D.Q. Pham, S. Liao, N. Sanpo, P. Kingshott, Christopher C. Berndt, V.K. Truong and A.S.M. Ang

Thermal sprayed antibacterial coatings: Hydroxyapatite and Sr-based materials

A. Methicillin-resistant *S. aureus* (MRSA-Gram positive bacteria)



- Bacterial attachment density on both coatings is similar. [a1 & b1 are similar]
- Sr-a can kill more MRSA bacteria than the HAp coating. [b2 shows more red than a2]
- Sr-b shows lower attachment of dead MRSA bacteria than HAp. [c2 shows less red than b2]

Summary #7

Sr-based composites: Excellent antibacterial properties, good biocompatibility by supporting stem cell adhesion and proliferation

Note: Gram positive bacteria have thick peptidoglycan cell walls. [12] Pham, D.Q. et al. (2020) 9/11

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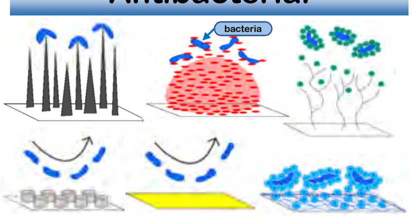
Relevancy to Thermal Spray & Surface Engineering for Antibacterial Applications

Take Home Messages

Thermal Spray

- Thermal spray is a recognized surface engineering technology for routine implementation into manufacturing.
- Many 'difficult-to-form' materials can be manufactured.
- The surface topography and bulk microstructure of thermal spray coatings can be designed.
- The surface and bulk chemistry can be deliberately created.

Antibacterial



- Design surface properties of interest; i.e., charge distribution, roughness, chemistry etc.
- Design topography by controlling spray parameters.
- Manufacture surfaces with embedded biocides.
- Combinatorial manufacturing processes to 'engineer the surface'.
- Control nature of voids (cracks & porosity).

Note: This presentation and slides(with supplementary material) is available on the SEAM web site. See <https://arcseam.com.au/latest-news/ > 10/11

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Supplemental Information

- References & information sources
- More detailed information for some slides
- Additional slides for consideration

Note: This presentation and slides(with supplementary material) is available on the SEAM web site. See <https://arcseam.com.au/latest-news/ >

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Summary of References and Web Site Links

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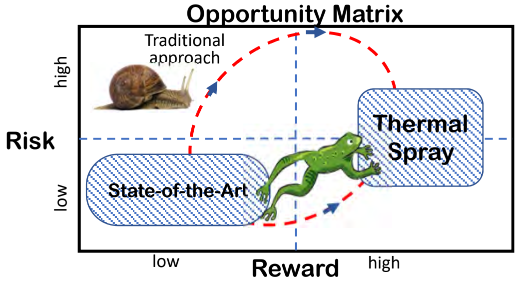
Take Home Messages: Surface Engineering Impacts of Thermal Spray are Positive

Summary #1
1. Biofilms & biofouling influence every aspect of society.
2. The key: Understanding the science of surface engineering.
3. The quest: Technological control of biofilms and biofouling.

Summary #2
4. Biofilms & biofouling are part of a continuum that represent biological growths that are differentiated by time, and propensity in size.

Summary #3
5. Surface roughness can be controlled.
6. Surface roughness influences biofouling.
7. Coating chemistry influences biofouling.
8. Successful new coating resists biofouling.

Opportunity Matrix



Summary #4
9. Cold spray of (i) 'metal + ceramic', & (ii) 'metal + ceramic + polymer' composites is a success.
10. Demonstration of surfaces that are antibacterial.
11. Antibacterial character ↑ with functional additive.

Summary #5
12. Opportunity: Coatings / films designed for focused functionality.

Summary #6
13. Chemical and mechanical strategies to kill bacteria.
14. Surface science and engineering knowledge is essential.
15. Q. What is the role of thermal spray science?

Summary #7
16. Sr-based composites: Excellent antibacterial properties, good biocompatibility by supporting stem cell adhesion and proliferation.

Summary #8
17. Thermal spray provides correct chemistry and morphology.

Summary #9
18. Physics spinoff: Fluids modeling of thermal spray and virus distribution is comparable.

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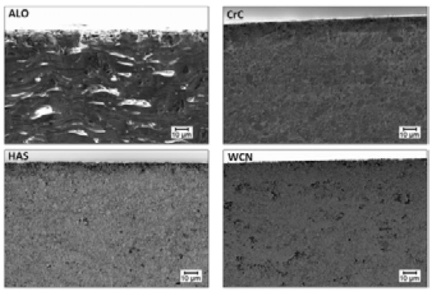
D.Q. Pham, S. Liao, N. Sanpo, P. Kingshott, Christopher C. Berndt, V.K. Truong and A.S.M. Ang

'High Velocity Oxygen Fuel' Carbide-Based Coatings: Marine Biofouling

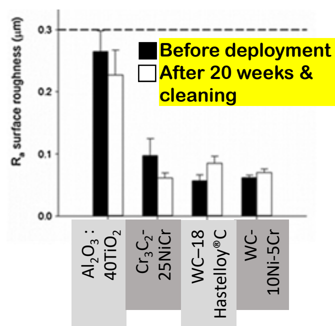
Feedstocks and Coating Microstructure

APS feedstocks (5–45 μm) = Al_2O_3 : $40TiO_2$ (ALO).
HVOF feedstocks of 15–45 μm
- Cr_3C_2-25NiCr (CrC)
- WC–18 Hastelloy®C (HAS)
- WC-10Ni-5Cr (WCN)



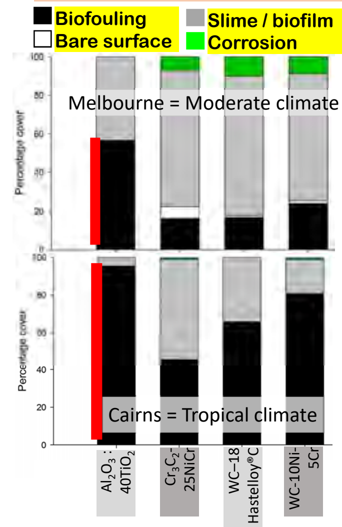
Summary #3
- Surface roughness can be controlled.
- Surface roughness influences biofouling.
- Coating chemistry influences biofouling.

Surface Roughness (Ra, μm)



- Al_2O_3 : $40TiO_2$ samples exhibited highest roughness.
- Cr_3C_2-25NiCr (~ half of ALO)
- WC–18 Hastelloy®C & WC-10Ni-5Cr showed lowest Ra.

Macrofouling



Al_2O_3 : $40TiO_2$ → higher fouling relative to HVOF.

[5] Piola, R. et al. (2018) 15 /11

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Cold Sprayed Coatings against *E. coli* Bacteria

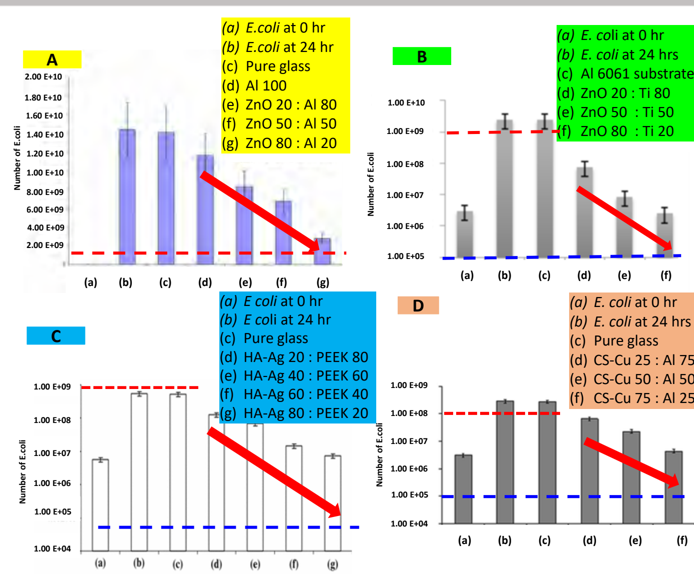
A. ZnO : Al Coatings on glass slides: The antibacterial activity ↓ with ZnO concentration.

B. ZnO : Titanium Coatings on Al 6061: The antibacterial activity ↑ with ZnO content.

C. Hydroxyapatite-Ag : PEEK Coatings on glass slides: The antibacterial activity ↑ with HA-Ag nanopowder.

D. Chitosan-Cu : Al Coatings on glass slides: The antibacterial activity ↑ with CS-Cu content.

Summary #4
- Cold spraying of (i) 'metal + ceramic', & (ii) 'metal + ceramic + polymer' composite is a success.
- Demonstration of surfaces that are antibacterial.
- Antibacterial character ↑ with functional additive.



[6] Sanpo, N. et al. (2008) [7] Sanpo, N. et al. (2010)
[8] Sanpo, N. et al. (2009a) [9] Sanpo, N. et al. (2009b)

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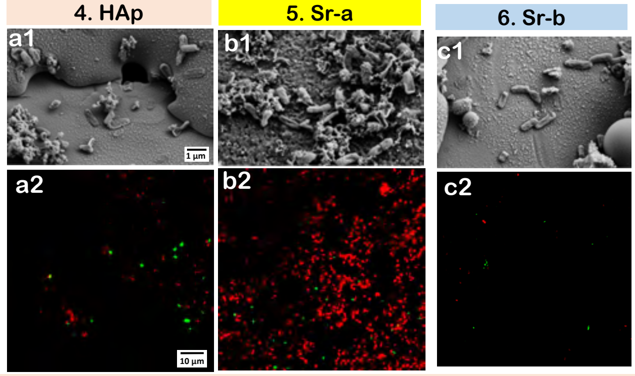
D.Q. Pham, S. Liao, N. Sanpo, P. Kingshott, Christopher C. Berndt, V.K. Truong and A.S.M. Ang

18 June 2020

Thermal sprayed antibacterial coatings: Hydroxyapatite and Sr-based materials

B. Response to 'Gram negative' bacteria. *P. aeruginosa*

4. HAp	5. Sr-a	6. Sr-b



LIVE

DEAD

- Live bacteria remained on the HAp coating. [a2 shows more green than b2 & c2]
- Bacterial attachment on Sr-a coating shows higher density. [compare b1 to a1]
- Bacteria were mostly killed on Sr-a coating. [b2 shows more red than a2]
- Bacteria were mostly killed on Sr-b. [c2 shows less red than a2 & b2]

<u>Summary #7</u>

Sr-a and Sr-b: Excellent antibacterial properties, good biocompatibility by supporting stem cell adhesion <u>and</u> proliferation

Note: Gram negative bacteria have a thin peptidoglycan layer sandwiched between two membranes.

[12] Pham, D.Q. et al. (2020)

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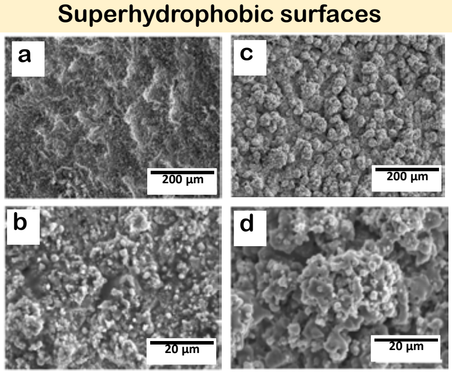
Antimicrobial Coatings using Thermal Spray for Biomedical Applications

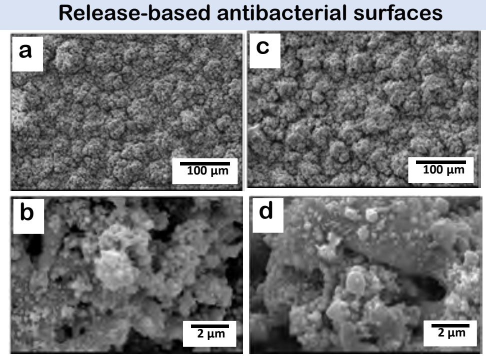
Superhydrophobic surfaces



Solution thermal spray of TiO_2 (< 500nm):
- (a) & (b) water-based suspension
- (c) & (d) ethanol-based suspension.

Superior water repellence (water contact angles ~ 167°) and improved mobility (water sliding angles ~ 1.3°).

Release-based antibacterial surfaces



Solution thermal spray of zinc-doped HAp:
- (a) & (b) HA + 5Zn < (c) & (d) HA + 10Zn

Antibacterial effects against *E. coli* and *S. aureus*

<u>Also</u>
- Twin wire arc spray of copper
- Flame spray of HAp doped Ag

Note: STS = solution thermal spray

[13] Sharifi, N. et al. (2016) [14] Kocaman, A. et al. (2019)
[15] Noda, I. et al. (2009) [16] Sergi, R. et al. (2018)

<u>Summary #8</u>

Thermal spray provides correct chemistry and morphology

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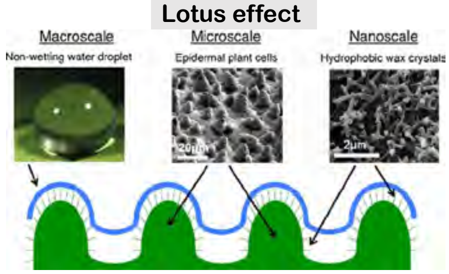
18

Desirable Characteristics of Thermal Spray Coatings for Antimicrobial Applications

Lotus effect



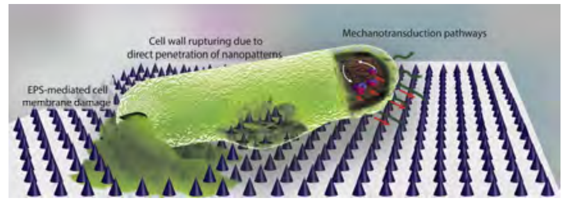
Bacteria Repelling Based Methods

- Charged surfaces: Adhesion of bacteria is discouraged on negatively charged surfaces.
- Superhydrophobic surfaces: Decrease the adhesion force between bacteria and the surface to remove of initially adhered bacteria (lotus effect).

Relevancy to Thermal Spray & Surface Engineering

- Measure surface properties of interest
- Encourage surface charges via electrophoresis
- Combinatorial manufacturing processes

Nanopatterned structure



Active killing based methods

- Release-based antibacterial surfaces: Biocides loaded in porous coatings and are released over time, i.e. Zn, Cu, Ag ions.
- Nanopatterned surfaces: Nanopatterns and surface textures with desired dimensions and morphologies on surfaces (nanotubes, nanowires).

Relevancy to Thermal Spray & Surface Engineering

- Manufacture surfaces with embedded biocides
- Control nature of voids (cracks & porosity)
- Design topography by controlling spray parameters

[17] Hobæk, T. C. et al. (2011)
[18] Olmo, J. A.-D. et al. (2020)

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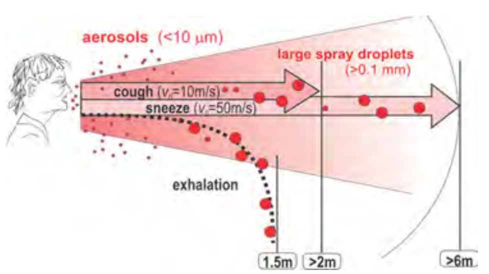
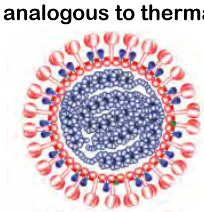
Sizes of Droplets & Aerosols: The Chemistry, Physics and Engineering Sciences

(a) The physics of thermal spray manufacturing is analogous to virus distribution

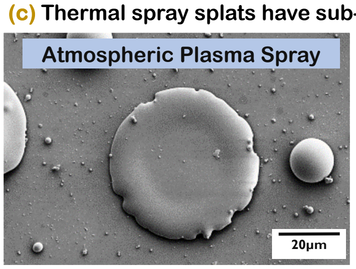


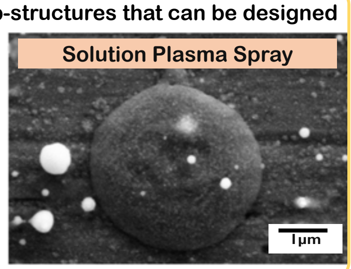
(b) The Coronavirus is nano-sized (60-140 nm). The aerosol droplets are '100 um composites of the Coronavirus'. This is analogous to thermal spray feedstocks.



Coronavirus
0.06 - 0.14 microns
(SARS-CoV-2)

(c) Thermal spray splats have sub-structures that can be designed





Summary #9

- Physics spinoff: Fluids modeling of thermal spray and virus distribution is comparable
- Thermal spray provides correct chemistry and morphology (from Summary #9)

[19] Image courtesy of Medium
[20] Image courtesy of Fast Life Hacks
[21] Photo courtesy of Condair Group
[22] Pham, D.Q. et al. (2019)
[23] Sanpo, N. et al. (2013b)

D.Q. Pham, S. Liao, N. Sanpo, P. Kingshott, Christopher C. Berndt, V.K. Truong and A.S.M. Ang

18 June 2020

Script for:

Bio-engineering Applications for Thermal Spray Coatings: Challenges and Opportunities

Slide #1:

Colleagues, thank you for the opportunity to present on behalf of an extensive R&D Team.

My name is Chris Berndt and the points of contact for this presentation are Mr Pham and Dr Ang.

Our presentation addresses the Challenges and Opportunities that Thermal Spray offers for Bacterial Mitigation.

It addresses surface engineering and manufacturing … and how these intersect with biological sciences.

Slide #2:

First of all: Please join me in Dedicating this presentation to the 'Health Care Staff' and 'Essential Service Personnel', who have been at the front line in addressing the COVIT-19 pandemic.

We acknowledge their generous devotion and dedication, which has been truly inspirational. We applaud you!

Slide #3:

As the first speaker for this global event, it is important to ‘set the scene’ and emphasise the critical nature that biofilms and biofouling play in our every day lives.

Slide #3 illustrates where the biological interface with the local environment can lead to poor medical or industrial outcomes.

The Table lists three manufacturing sectors that exemplify a cross section of societal needs. Some summary points follow:

One - Infectious biofilms impact health, our quality of life, and life style. For instance, if you have a tooth ache, then you have experienced the adverse influence of a biofilm.

Two - Industrial biofouling impacts ‘the bottom line’ of productivity. If you experience clogged drain pipes .. there is the likelihood that biofouling is the cause.

Thus, the first summary states that our aim as technologists is to control biofilms and biofouling by understanding their science.

Slide #4:

So let us define and distinguish biofilms from biofouling, Slide #4. Both mechanisms represent a continuum of biological growth.

The figure shows a transition over time from <u>reversible</u> adhesion of bacteria, shown as a green period measured in seconds; to <u>irreversible</u> adhesion of bacteria, shown as the red period that extends to months.

An important point is that biofilms overlap the reversible and irreversible adhesion regimes.

Thus, and this is the take home message, if bacteria attachment can be controlled by clever surface engineering, then the films and fouling mechanisms can be disrupted.

Thermal spray coatings have demonstrated this ability to be disruptive, as will be described in the following discussion.

Slide #5:

The disruptive nature of advanced thermal spray manufacturing is shown on Slide #5 for a high velocity oxygen fuel coating.

This collaborative work was sponsored by the Defence Materials Technology Centre. The industrial customer dictated the need for a superior wear and corrosion resistant surface for marine environments.

The existing benchmark was an atmospheric plasma sprayed alumina-titania coating.

This coating exhibited a roughness of 0.26 micrometre Ra.

This coating was susceptible to severe biofouling in both moderate and tropical seas, as indicated by the red columns on the two graphs after 20-weeks of immersion.

The success of this work was founded on a composite feedstock that was designed to have (i) high deposition efficiency, (ii) low as-sprayed roughness, (iii) ability to be super-finished, and (iv) excellent corrosion-wear characteristics.

We were successful in reducing the biofouling significantly because the intrinsic surface characteristics were customised for this application. This is shown by the dramatic decrease in ‘percentage cover of biological growths’ in marine environments as shown by the blue columns.

Slide #6:

Thus, we have learned how to interrupt the mechanism of bacteria attachment and Slide #6 shows results for cold sprayed coatings of four materials that have been composited with an antibacterial agent.

The results for zinc oxide with aluminium metal are shown in yellow. The antibacterial nature is demonstrated.

The supplemental slides to this presentation show further data for the green, blue and orange composites.

The point is that we have tested a wide range of ‘metal + ceramic’ & ‘metal + ceramic + polymer’ materials. In all instances, the *E. coli* decreases with the addition of the antibacterial agent. This is good news that is summarized at the bottom of Slide #6.

Slide #7:

Antibacterial materials can also be thermal sprayed by employing liquid feedstocks as shown in Slide #7.

The chelating (**kee-lating**) agent of polyvinyl alcohol (PVA -[CH2CH(OH)]n), citric acid (CA - C6H8O7), or oxalic acid (OA - C2H2O4) has been used.

These chelating (**kee-lating**) agents react with the cobalt ferrite nanoparticles to form a stable water-soluble complex ….. that is used as feedstock for liquid thermal spraying.

The deposit forms a characteristic splat where the surface roughness depends on the chemistry of the liquid feedstock … as indicated by the topographic features shown in the central panel. The major outcome is that *E. coli* survival is significantly reduced.

Thus, coatings and films can be designed for antibacterial functionality.

Slide #8:

It becomes apparent that there are several mechanisms for effective antibacterial and anti-biofouling outcomes, Slide #8.

The bacteria are represented as blue ellipses. These bacteria interact with a surface that has distinctive chemical, physical, electrical and topological features.

Now here is, literally, the million dollar question (do I have your attention?).

I ask you to prioritize these 7 surfaces in order of their spray capability.

That is, 'Can thermal spray create such desirable surface features and bulk architectural morphologies?'

This is the Opportunity and Challenge that is referenced in the title of this presentation.

My short answer is "An emphatic yes." Yes…thermal spray has the ability to create such features .. .as well as other interesting microstructural artefacts.

The longer answer, for discussion purposes, is mechanism #1 takes advantage of intrinsic porosity and crack networks; mechanisms #2 & #5 take advantage of nano-particles and knowledge concerning spray tables; and mechanisms #4, #6 and #7 can be referenced back to the Van der Waals adhesion mechanisms posed by Profs. Matting and Steffens in the mid-1940s.

Some of these mechanisms have been operative in the case studies shown in the earlier slides.

Slide #9:

A very recent case study is shown in Slide #9. Three materials have been thermal sprayed: the traditional hydroxyapatite and two strontium-based materials of different chemistries.

The top 3 scanning electron micrographs show *S. aureus* bacteria on the surfaces of these substrates.

The bottom 3 images show the microbiological results. These tests are unfamiliar to a traditional thermal sprayer …. so let me explain the simple interpretation:

(i) Green represents live bacteria & red shows dead bacteria.

(ii) The red color is most desirable since we desire an anti-bacterial response.

(iii) The proportion of the colours represent the relative adhesion of bacteria.

Therefore, the biological interpretation of these results can be simplified as:

(i) The strontium-a and strontium-b materials kill bacteria to a greater extent than hydroxyapatite.

(ii) Material strontium-b has less adhering bacteria than strontium-a.

So a major outcome of this R&D is that there are alternatives to traditional thermal sprayed hydroxyapatite on the near term horizon.

Slide #10:

As we draw to a close, let me present some key ‘Take Home Messages’, Slide #10.

First: Thermal spray is a recognized manufacturing technology. A vast array of ‘impossible materials’ can be sprayed as films and coatings. The bulk structure and surface properties can be deliberately designed for specific functionalities.

The bottom blue box refers to antibacterial needs. The focus is that these mechanisms (and other desirable surface attributes) can be tailored on the basis of thermal spray science.

Hence: Again referring back to the title of this talk: ‘The Challenges and Opportunities’ are immense and ready for harvesting.

Slide #11:

In closing this presentation, the authors thank the Thermal Spray Society Leadership for their vision in organising this Global Event. Their foresight and planning is appreciated!

We can also plan for the day when we present the longer talk in a face-to-face environment.

Finally: Our R&D is a Team Sport! Many disciplines, many universities, many labs, many cultures, many companies. We are always open to collaboration since our Team believes that 'We are stronger when we work together.'

Keep well & Keep safe!

Thank you.

🙏