New zincophobic coatings for hooks/jigs: a way to reduce cost and environmental impact in batch hot-dip galvanizing

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Aleksandra Cieplak, David Balloy

Univ. Lille, CNRS, INRAE, Centrale Lille, UMR 8207 - UMET - Unité Matériaux et Transformations, F-59000 Lille, France

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Partners of the project

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EN GÉNIE DES MATÉRIAUX

SATT Nord

AXIMUM

Aleksandra CIEPLAK

- 3rd year **PhD student in Materials Chemistry** at University of Lille
- **Masters Degrees in Chemistry and Materials Chemistry** at Ecole Nationale Superieure de Chimie de Lille and University of Lille

David BALLOY

- **Professor** at University of Lille, Polytech'Lille
- **Researcher** in the domain of casting, reactivity of metals in severe environments and metal recycling at UMET laboratory

Context of the study – batch galvanizng

Galvanizing cycle

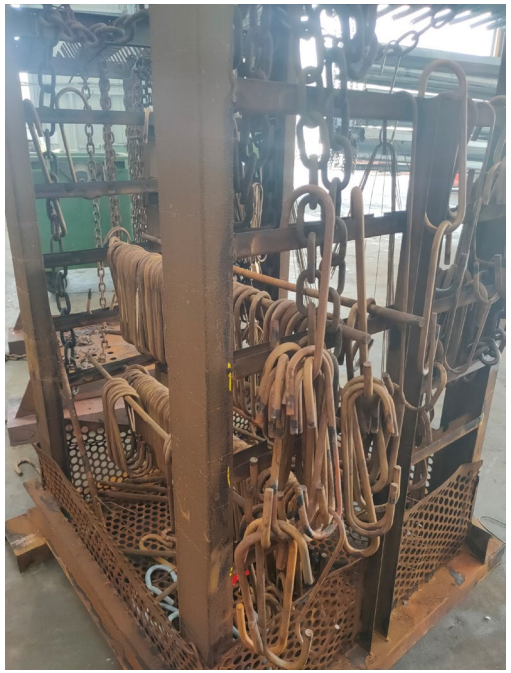
- Hanging of parts
- Degreasing (base)
- Stripping (acid)
- Fluxing (reductant)
- Galvanizing (liquid Zn)
- Unhooking of parts
- Cleaning of hooks (acid)

x N cycles

Holders

Problems with cycling galvanizing of holders

- **Corrosion** of steel (intermetallics' formation and their dissolution during stripping)
- **Deposition of zinc at the surface** during emersion



→ Economical and ecological costs

Protective materials in continuous galvanizing

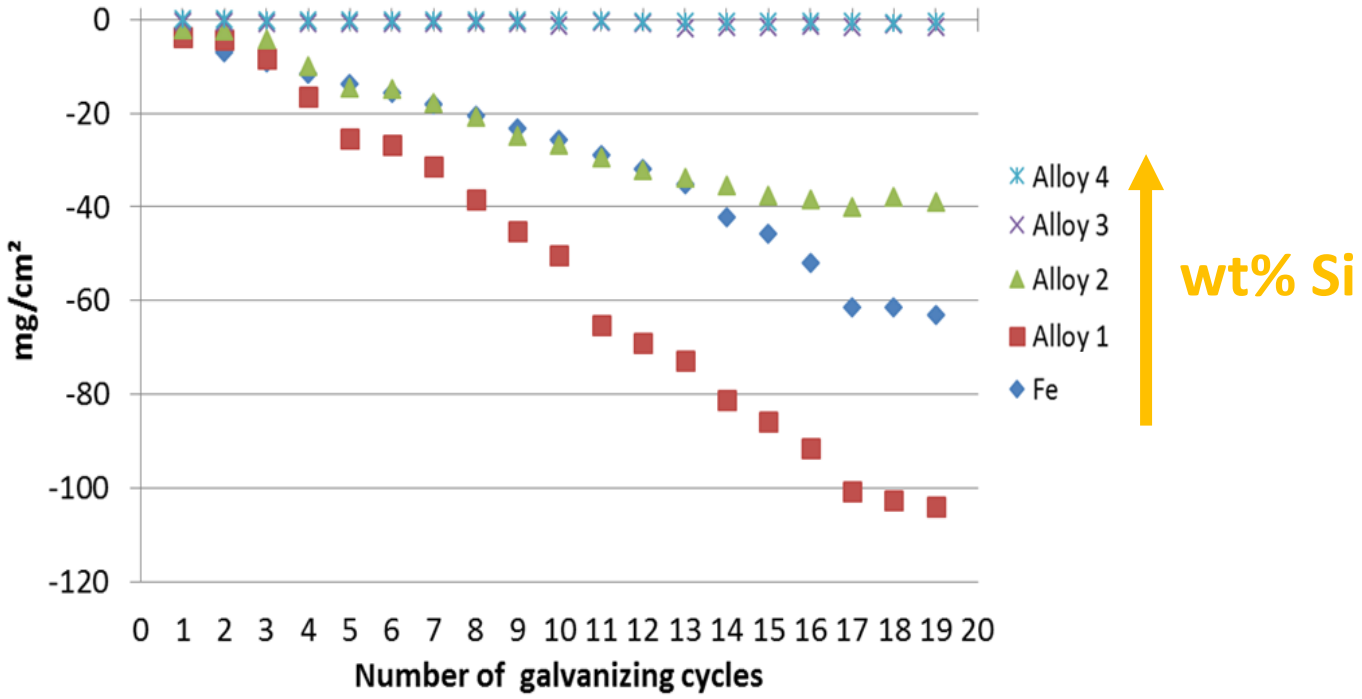
316L stainless steel	Ceramic coatings and borides	Ti or Co based alloys
• Resistant to the thermal shock • Wetted by liquid Zn • Increased cost of structures (steel 720€/t, SS 3 370€/t*)	• Non-wetted by liquid Zn • Brittle • Non-resistant to thermal shock	• Very high cost of material (Ti: 4790€/t, Co: 45000€/t*)

*Prices for 02/2023

- X. Ren, X. Mei, J. She, J. Ma, Materials Resistance to Liquid Zinc Corrosion on Surface of Sink Roll, Journal of Iron and Steel Research, International, 14 (5), 2007, 130-136
- S. Ma, J. Xing, H. Fu, D. Yi, J. Zhang, Y. Li, Z. Zhang, B. Zhu, S. Ma, Interfacial morphology and corrosion resistance of Fe–B cast steel containing chromium and nickel in liquid zinc, Corrosion Science, 53 (9), 2011, 2826-2834
- J. Xu, X. Liu, M. Bright, J. G. Hemrick, V. Sikka and E. Barbero, Reactive Wetting of an Iron-Base Superalloy MSA2020 and 316L Stainless Steel by Molten Zinc-Aluminum Alloy, Metall Mater Trans A, 39, 2008, 1382-1391

FeSi alloy resistance to molten zinc

Bulk material



- Weight loss of bulk Fe-Si materials in function of galvanizing cycles

- No zinc corrosion observed for wt% Si > 20%
- Bulk FeSi too brittle
- Thermodynamic difficulties to form FeSi(20%wt) coating by fusion of the Fe-Si powder

OUR SOLUTION

Fabrication of studied coatings

SLURRY process

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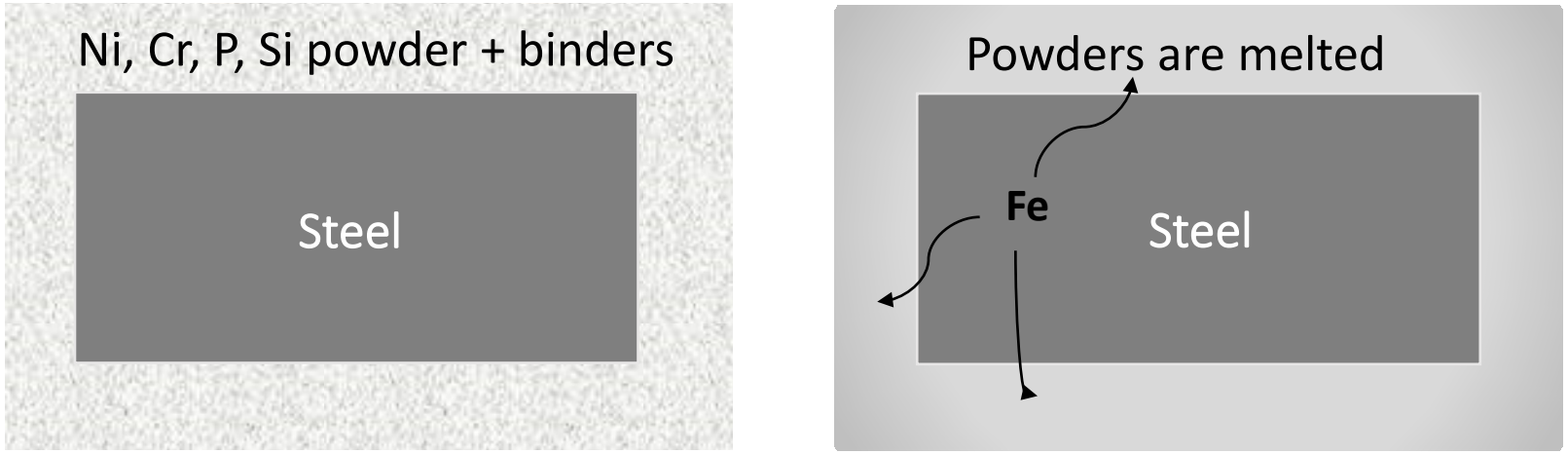
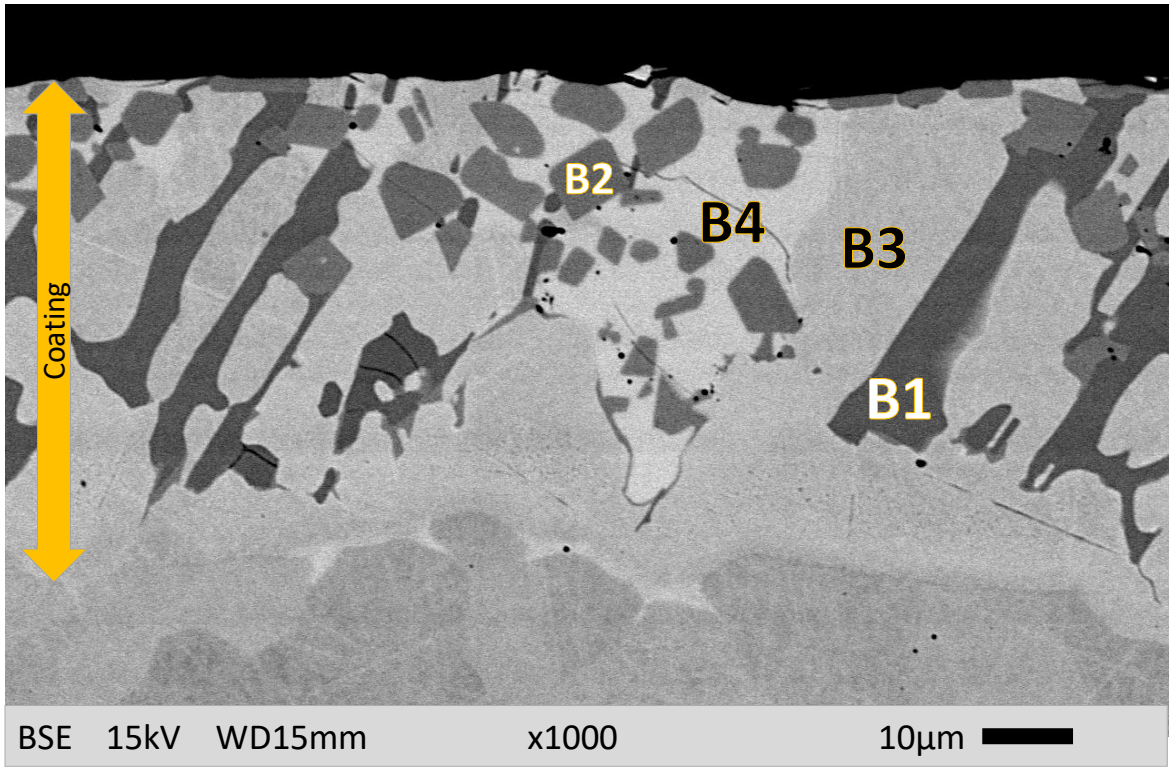
- ✓ Uniform thickness of the coating
- ✓ Nature of the steel/coating interface formed by diffusion makes is **resistant to the thermal shock**

High temperature treatment



- Slow cooling
- Controlled atmosphere

Zincophobic coating

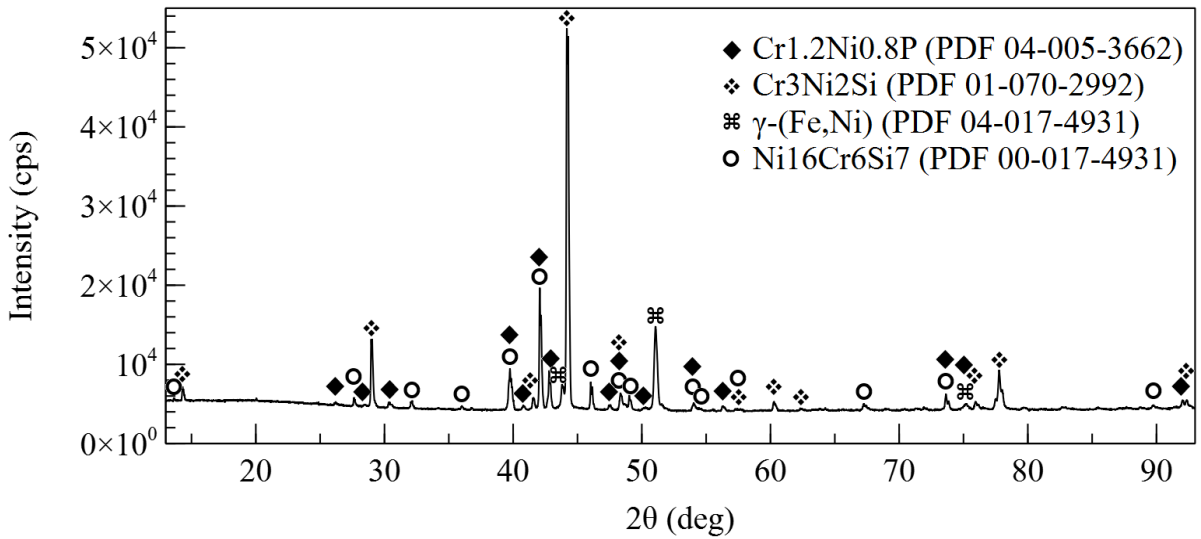


- SEM-BSE image of the zincophobic coating

Thickness ≈ 50 µm

HYPOTHESIS

Formation of a very thin protective oxide layer at the surface

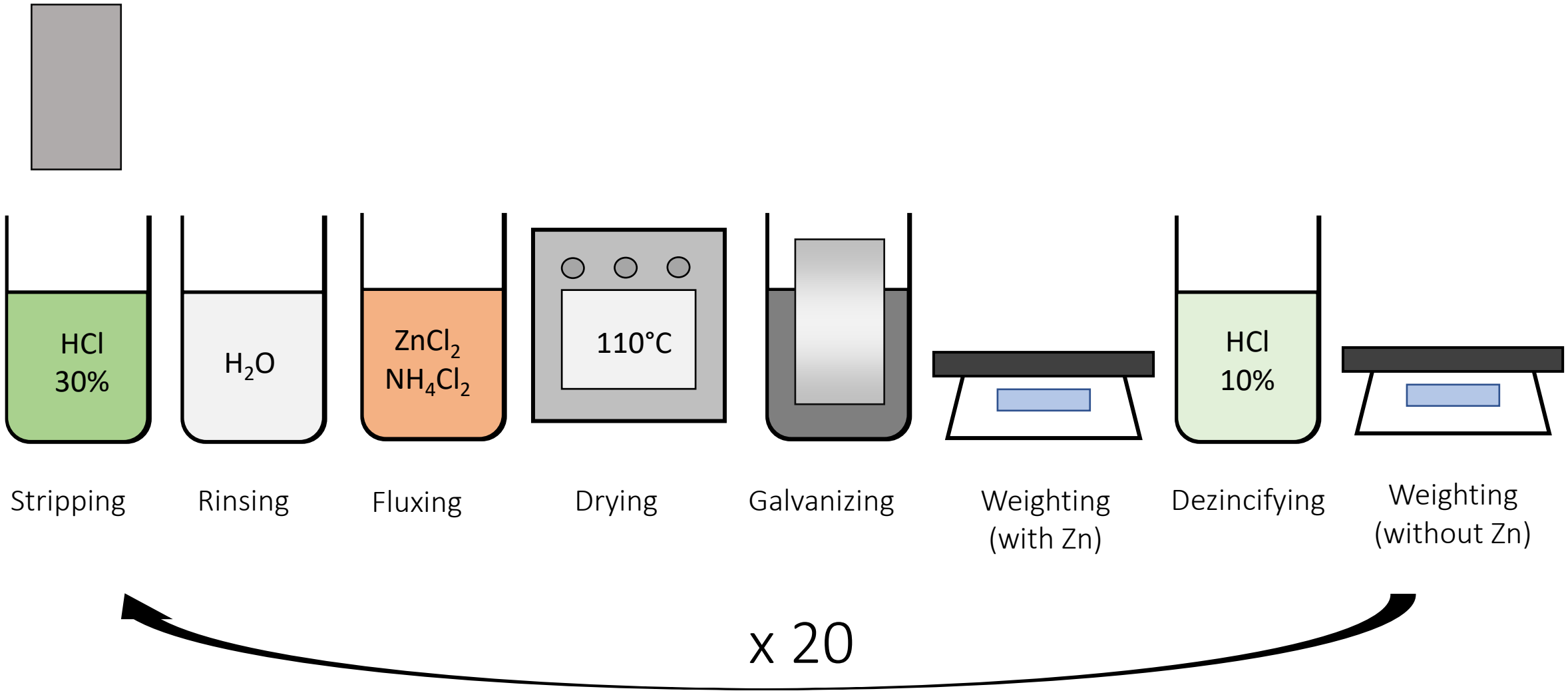


- Zincophobic coating's diffractogram

Phase	Si	P	Cr	Mn	Fe	Ni
B1	2.6	**19.1**	34.9	0.1	17.4	25.9
B2	8.4	1.2	**48.4**	0.1	3.6	38.4
B3	6.3	0.2	12.7	0.1	34.4	46.4
B4	10.9	4.2	12.2	0.3	11.4	60.9

- Coating's composition analysed by EPMA (%wt)

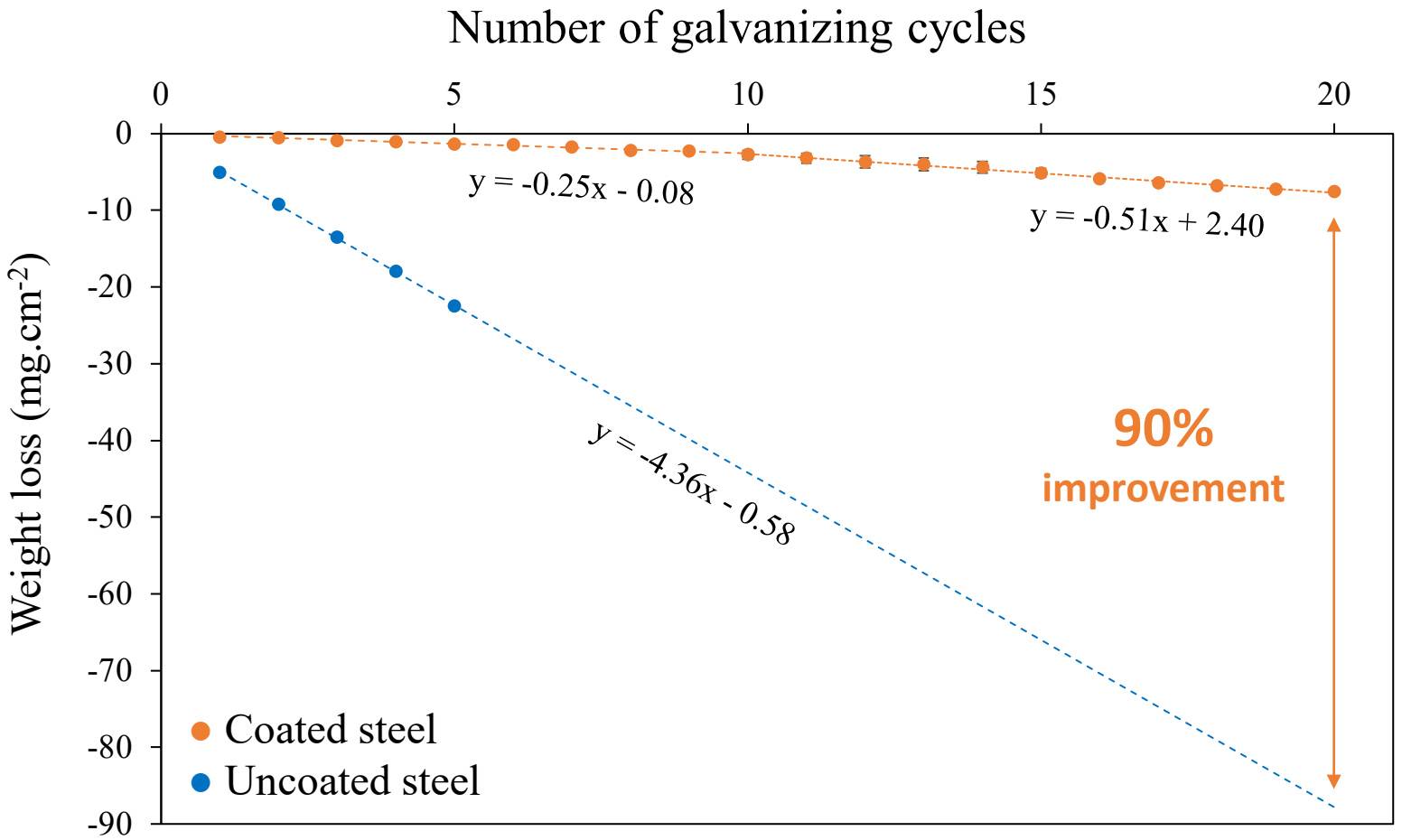
Experimental procedure



RESULTS

Cyclic galvanizing tests

Steel corrosion by liquid zinc



- Composition of uncoated steel (DD13) (wt%)

C	Mn	P	S
Max 0.08	Max 0.4	Max 0.03	Max 0.03

- Zn bath follows the ISO 1461 norm (additional elements: Al - 0.1%, Pb - 0.8%, Sn – 0.2%, Ni - 0.02%)

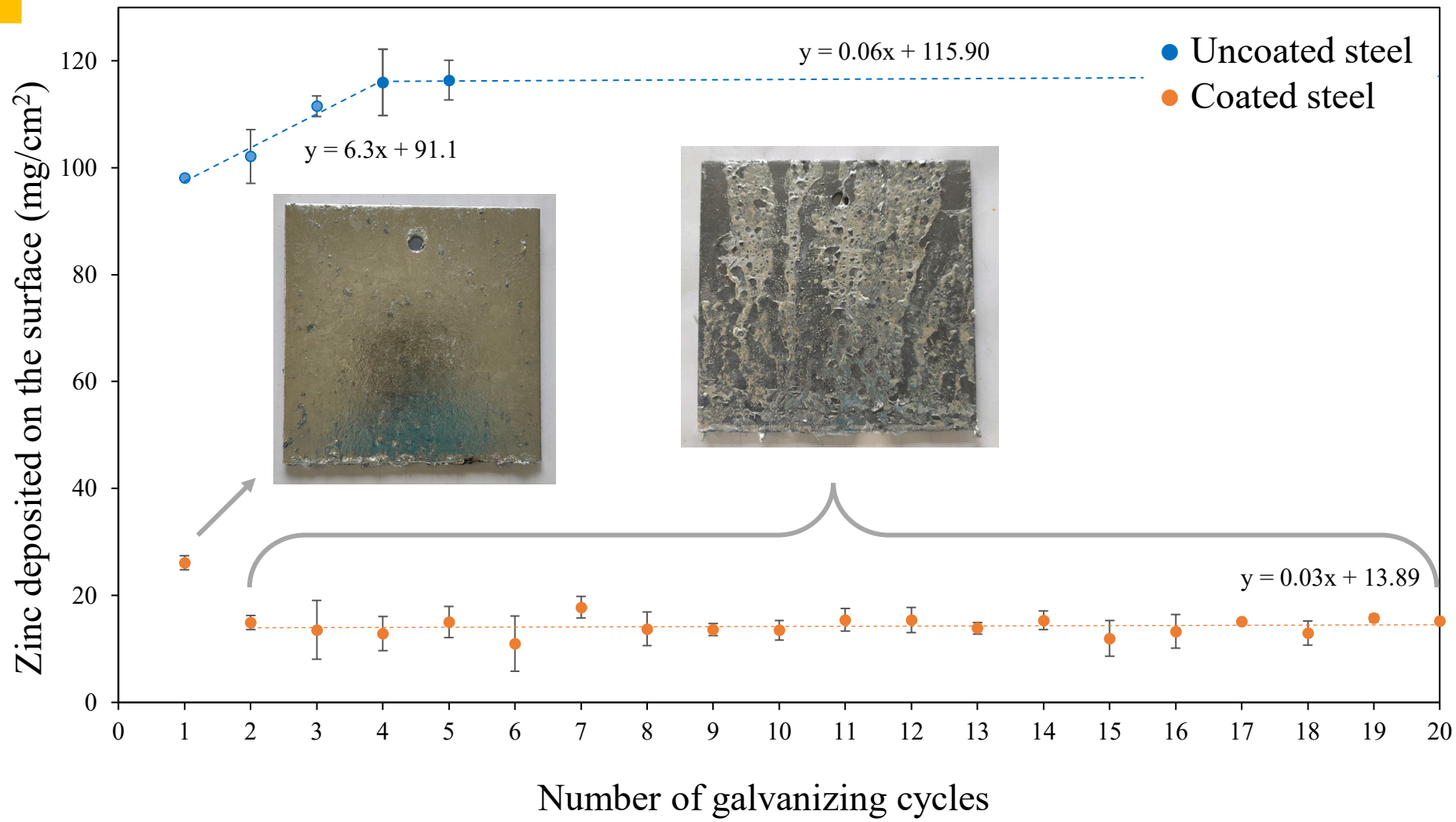
Cyclic galvanizing tests

Zinc deposition

85% of zinc savings after 20 cycles

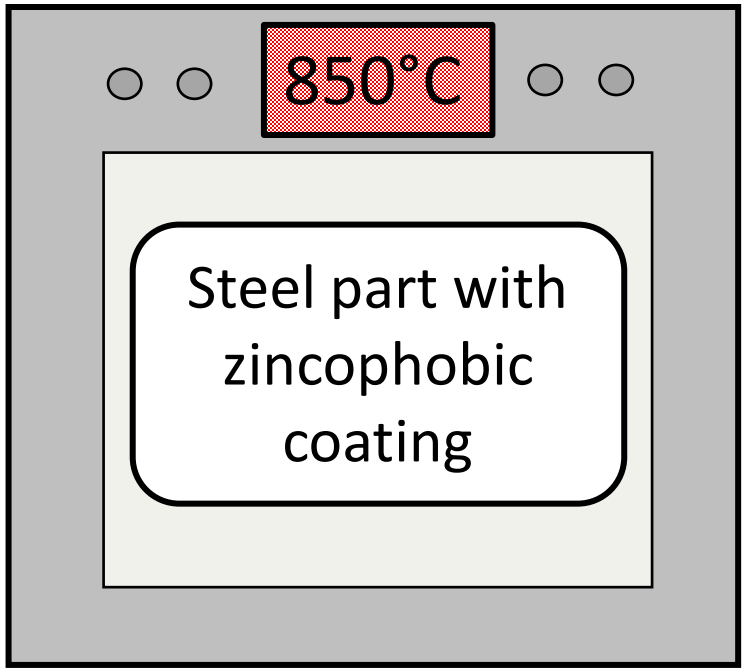
1 cycle of conditionning before the best behavior is achieved

Sample size:
10x10x0,3 cm



IMPROVEMENTS

Preoxidation



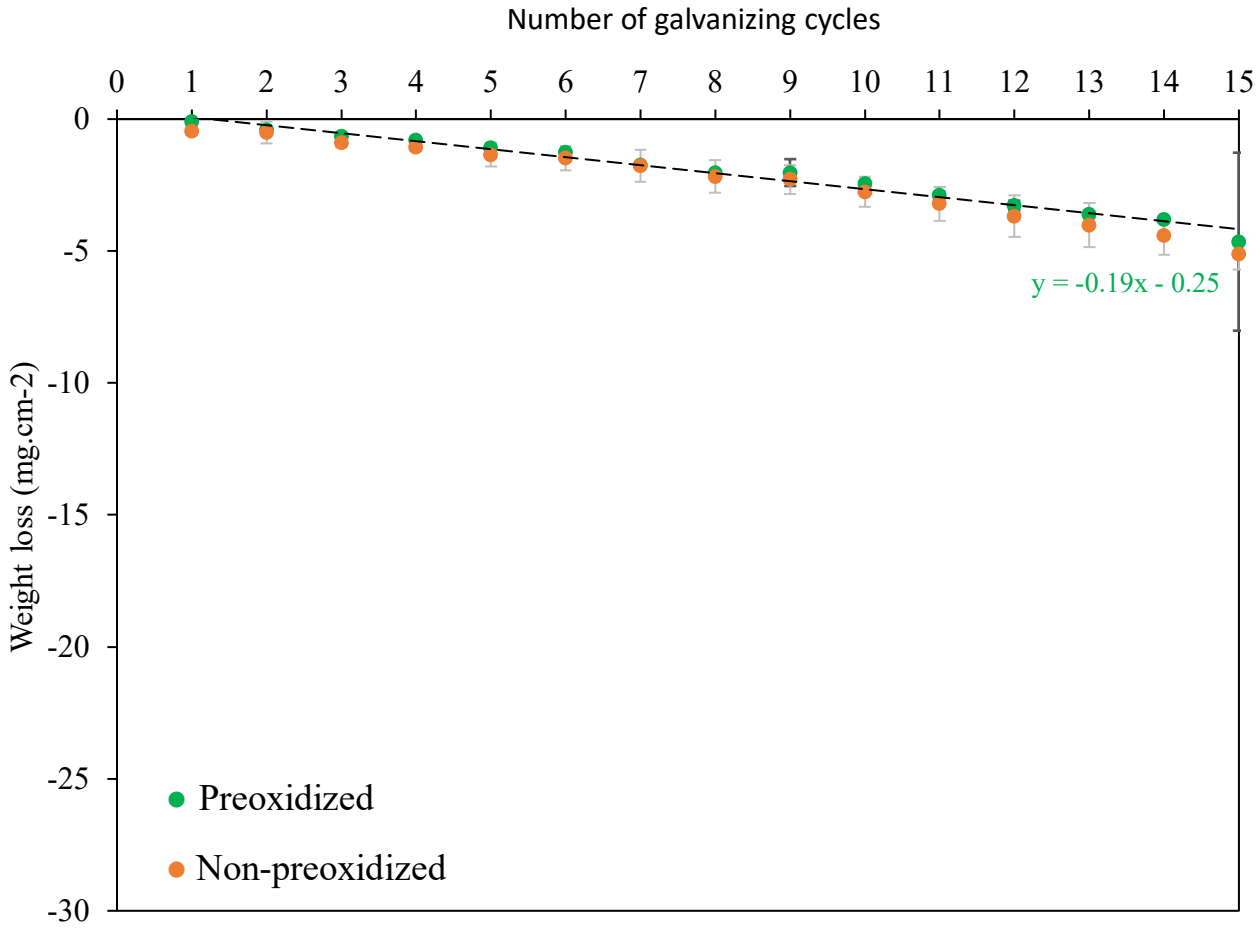
1H

Generation of the protective, **non-wetting** oxide at the surface

Preoxidation

Steel corrosion by liquid zinc

Small positive change of liquid zinc corrosion of coated steel if preoxidation applied



Corrosion rate for

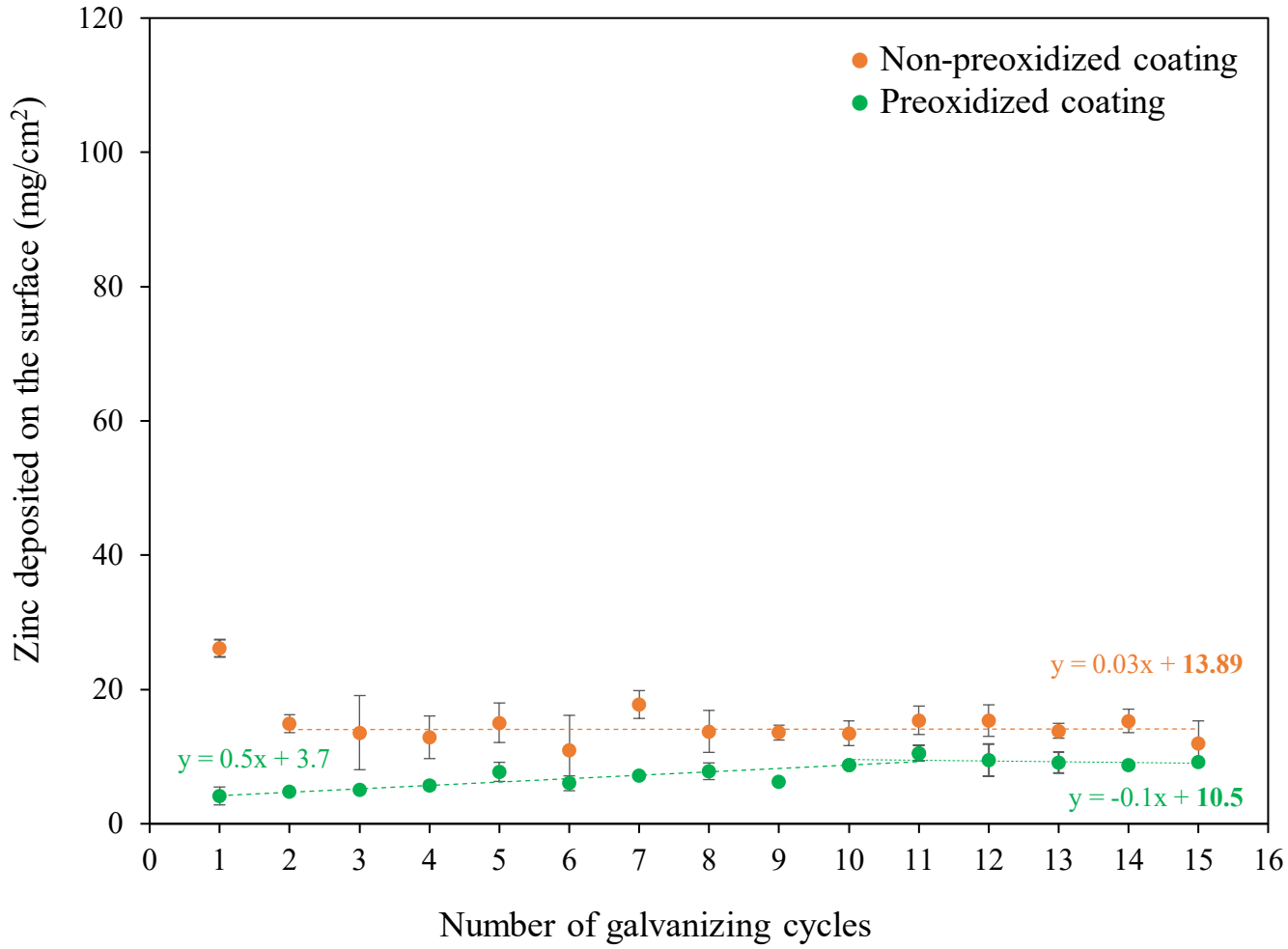
- Non-preoxidized coated steel: 0.25 $mg.cm^{-2}.cycle^{-1}$
- Preoxidized coated steel: 0.19 $mg.cm^{-2}.cycle^{-1}$

Preoxidation

Zinc deposition

- 85% less zinc on the sample after the first cycle
- Increase of settled zinc during first 10 cycles for preoxidized samples
- Stabilisation around 11th cycle at 10.5 mg/cm^2

  → 25% less zinc than for non-preoxidized samples



First industrial tests

AXIMUM

➢ 30 galvanizing cycles

- The industrial partner does not need to dezincify the hooks between cycles

✓ Gain of performance of the site

✓ Decreased use of acid bath and zinc waste treatment

Uncoated steel hook with Zn

Coated steel hook with Zn (30 cycles)

Conclusions and perspectives

- ✓ 90% decrease in weight loss of Fe-Cr-Ni-Si-coated steel in liquid zinc in comparison to an uncoated carbon steel
- ✓ Lower surface wetting and 85% zinc savings if coated-steel is used
- ✓ Preoxidation further decreases zinc adherence and has small positive influence on corrosion
- ✓ First industrial tests give positive results

→ Optimisation of preoxidizing conditions

Perspectives on the industrial development

✓ Patent application pending

→ Tests on different geometries of steel parts
→ Tests on the industrial scale and with bigger number of samples
→ Formation of partnerships with interested galvanizers and opening of a new industrial activity

✓ Contacts for industrialisation:

→ Bruno Gay, B.Circle: bruno.gay1801@outlook.com
→ Jean-Pierre Leac, SATT Nord: jean-pierre.leac@sattnord.fr
→ David Balloy, Université de Lille: david.balloy@univ-lille.fr

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Thank you for your attention!

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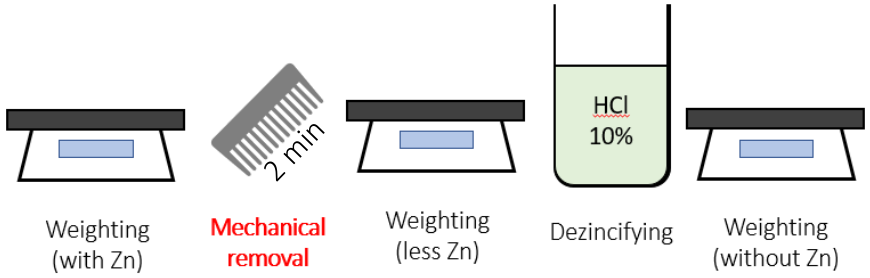
Preoxidation

Adhesion of zinc on coated samples



- About 10 % of zinc can be removed with small mechanical force on non-preoxidized samples
- Zinc on preoxidized samples is very easy to remove at first cycles, but the adhesion decreases following the **square root function**.