

# OPTIMIZATION OF ELECTROCHEMICAL DEPOSITION OF Zn-Mn-Al<sub>2</sub>O<sub>3</sub> COMPOSITE COATINGS

Mihael Bucko<sup>1</sup>, Marija Riđošić<sup>2,3</sup>, Milorad Tomić<sup>2</sup>, Jelena B. Bajat<sup>3</sup>

<sup>1</sup>University of Defence, Military Academy, 33 Veljka Lukića Kurjaka St, 11000 Belgrade, Serbia, [mbucko@tmf.bg.ac.rs](mailto:mbucko@tmf.bg.ac.rs)

<sup>2</sup>University of East Sarajevo, Faculty of Technology Zvornik, Karakaj 34A, 75400 Zvornik, Republic of Srpska, [mtomicc@yahoo.com](mailto:mtomicc@yahoo.com)

<sup>3</sup>Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia, [mridjosic@tmf.bg.ac.rs](mailto:mridjosic@tmf.bg.ac.rs), [jela@tmf.bg.ac.rs](mailto:jela@tmf.bg.ac.rs)



## INTRODUCTION

The Zn alloy coatings that have found the broadest application range, are Zn-Ni, Zn-Fe, Zn-Co, Zn-Sn and Zn-Mn alloy. On the other hand, the Zn composite coatings, obtained by using electroplating baths with various dispersive fine phases, which may be both hard phases, such as SiC, Al<sub>2</sub>O<sub>3</sub>, MoS<sub>2</sub>, TiO<sub>2</sub>, SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub>, and soft phases such as polytetrafluoroethylene (PTFE) or graphene. The improvement of different features of a composite coating depends mainly on the size and the percentage of the incorporated fine particles, as well as on their distribution in the metallic matrix [1-3]. This work focuses on the development of a novel Zn-alloy-composite coating, i.e. the coating that will benefit from the insertion of both an additional metal and a ceramic particle into the zinc matrix.

**THE AIM OF THE WORK:** probing the electrodeposition of Zn-Mn/Al<sub>2</sub>O<sub>3</sub> composite coatings from chloride bath and characterizing the obtained coatings in terms of their morphology and corrosion resistance.

## EXPERIMENTAL

□ **Plating parameters:** chloride additive-free plating baths, temperature of 25 °C, deposition current density: 1-5 A dm<sup>-2</sup>, agitation: magnetic stirring, ultrasound, Al<sub>2</sub>O<sub>3</sub> particles: 300 nm, 10 μm

□ **SEM/EDX, EIS, polarization measurements:** chemical content, morphology, corrosion resistance in 3% NaCl

## RESULTS AND DISCUSSION

### Influence of Mn<sup>2+</sup> : Zn<sup>2+</sup> ion ratio in the bath

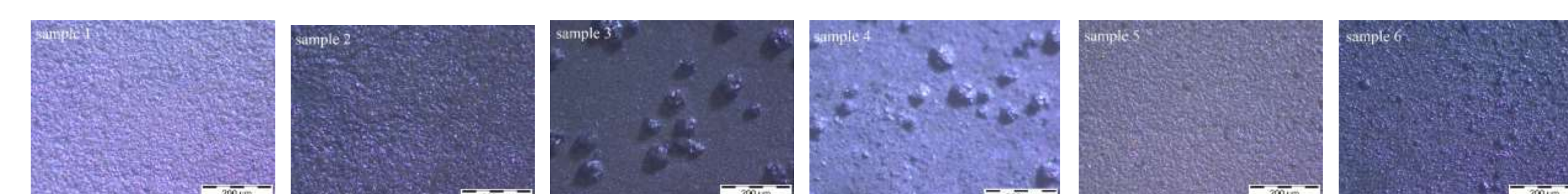
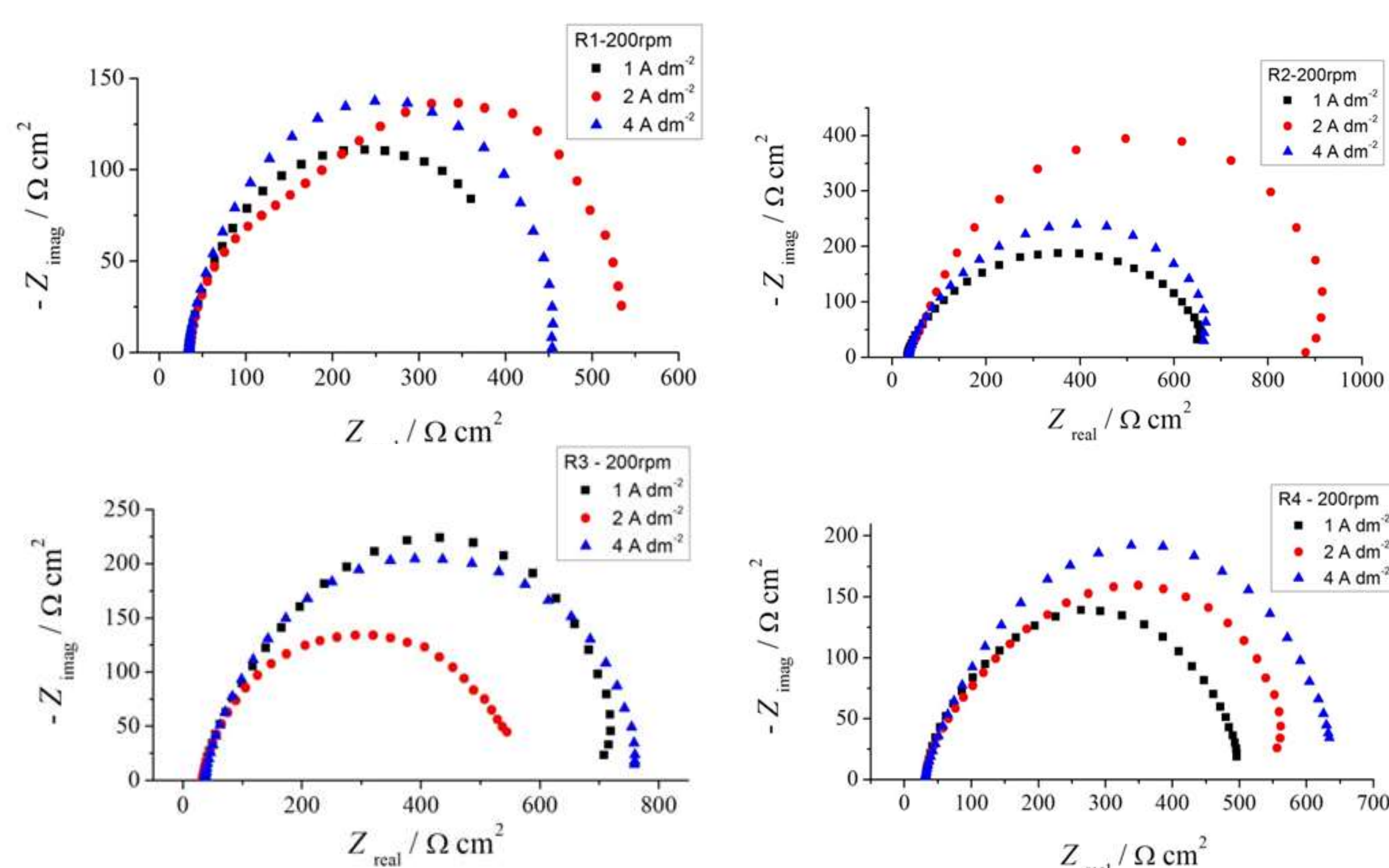
Plating bath	R1 (mol·dm <sup>-3</sup> )	R2 (mol·dm <sup>-3</sup> ) [Mn <sup>2+</sup> ]:[Zn <sup>2+</sup> ]=1:1	R3 (mol·dm <sup>-3</sup> ) [Mn <sup>2+</sup> ]:[Zn <sup>2+</sup> ]=1:2	R4 (mol·dm <sup>-3</sup> ) [Mn <sup>2+</sup> ]:[Zn <sup>2+</sup> ]=2:1
KCl	3	3	3	3
H <sub>3</sub> BO <sub>3</sub>	0,42	0,42	0,42	0,42
ZnCl <sub>2</sub>	0,45	0,45	0,45	0,45
MnCl <sub>2</sub> ·4H <sub>2</sub> O	-	0,45	0,25	0,9
Al <sub>2</sub> O <sub>3</sub>	1,00	1,00	1,00	1,00

10 μm Al<sub>2</sub>O<sub>3</sub> magnetic stirring, 1-4 A dm<sup>-2</sup>

### 1:1 Mn<sup>2+</sup> : Zn<sup>2+</sup>, 300 nm Al<sub>2</sub>O<sub>3</sub> particles

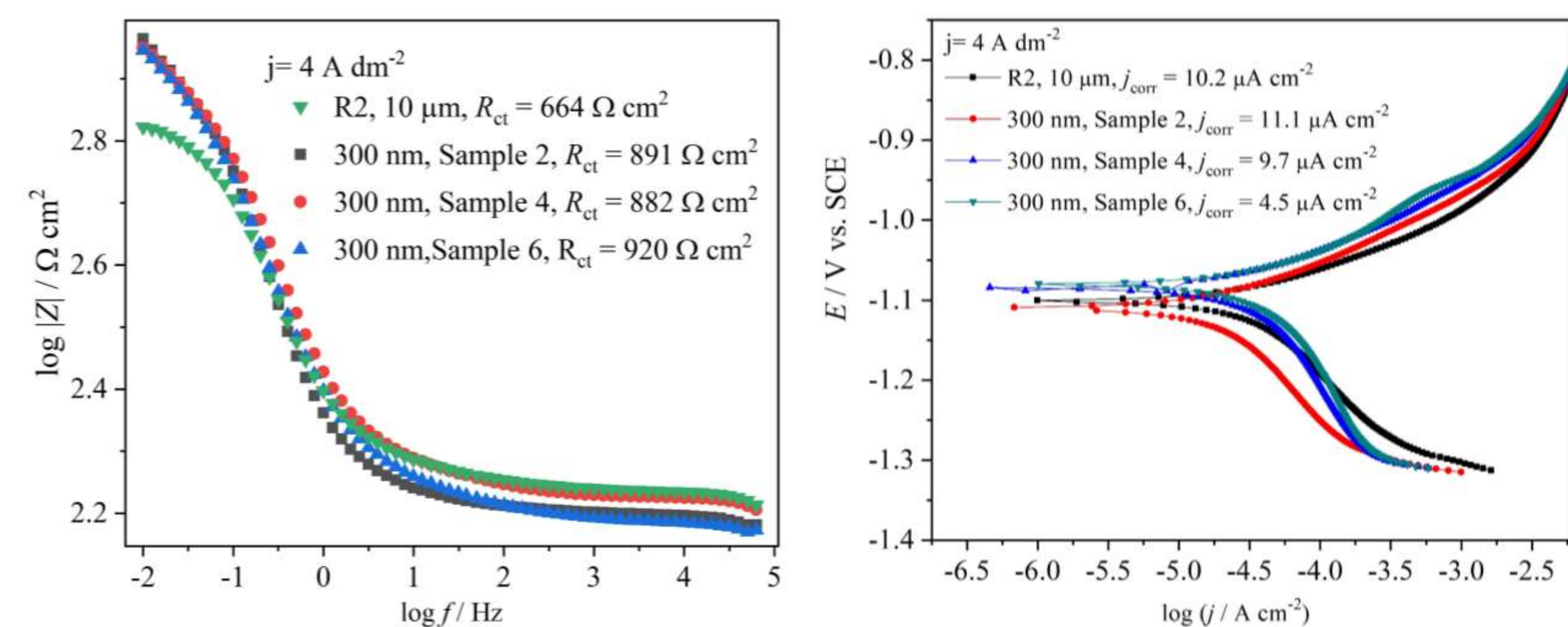
Sample No.	Deposition e.d.	Deposition conditions	wt.% Mn	wt.% Al	calculated wt.% Al <sub>2</sub> O <sub>3</sub>	wt.% O
1	5 A dm <sup>-2</sup>	magnetic stirrer	5.8	0	0	12.2
2	4 A dm <sup>-2</sup>	magnetic stirrer	5.2	0	0	11.5
3	5 A dm <sup>-2</sup>	magnetic stirrer + Al <sub>2</sub> O <sub>3</sub>	5.3	2.6	4.8	13.8
4	4 A dm <sup>-2</sup>	magnetic stirrer + Al <sub>2</sub> O <sub>3</sub>	4.7	2.4	4.5	11.0
5	5 A dm <sup>-2</sup>	ultrasound + Al <sub>2</sub> O <sub>3</sub>	5.9	1.0	1.8	12.8
6	4 A dm <sup>-2</sup>	ultrasound + Al <sub>2</sub> O <sub>3</sub>	4.9	0.7	1.3	9.7

### Electrochemical impedance spectroscopy



Optical images: all samples showed non-porous and compact structure formed by dissimilar grains

Comparison of corrosion performance of the coatings with alumina particles of different dimensions (10 μm or 300 nm)



### Conclusions:

The optimal parameters:

- 300 nm Al<sub>2</sub>O<sub>3</sub> particles
- [Mn<sup>2+</sup>]:[Zn<sup>2+</sup>]=1:1
- ultrasound agitation
- deposition c.d 4 A dm<sup>-2</sup>

### Morphology (optical images) : R2



1 A dm<sup>-2</sup>

2 A dm<sup>-2</sup>

4 A dm<sup>-2</sup>

### Chemical content

Mn: 0,075 – 1,0 wt %  
Al: 0,14 - 4,0 wt. %

**R2, R3, 4 A dm<sup>-2</sup>: the highest corrosion stability**  
**4 A dm<sup>-2</sup> the most homogenous morphology**

### References

- F. C. Walsh, C. Ponce de Leon, A review of the electrodeposition of metal matrix composite coatings by inclusion of particles in a metal layer: an established and diversifying technology, *Trans. IMF* 92 (2014) 83-98.
- H. Zheng, M. An, J. Lu, Corrosion behavior of Zn-Ni-Al<sub>2</sub>O<sub>3</sub> composite coating, *Rare Metals* 25 (2006) 174–178.
- B.M. Praveen, T.V. Venkatesha, Electrodeposition and properties of Zn-Ni-CNT composite coatings, *J. Alloys and Compounds* 482 (2009) 53-57.

### Acknowledgements

This research was financed by the Ministry of Education, Science and Technological Development, Republic of Serbia (Contract No. 451-03-9/2021-14/200135 ) and Ministry for Scientific and Technological Development, Higher Education and Information Society of the Republic of Srpska (Contract No. 19.032/961-38/19).