

# PROTECTIVE AND SELF-HEALING PROPERTIES OF CERIUM-MODIFIED MOLYBDATE CONVERSION COATING ON STEEL

Aliona Kirdeikienė<sup>1</sup>, Olga Girčienė<sup>1</sup>, Laima Gudaviciūtė<sup>1</sup>, Vitalija Jasulaitienė<sup>1</sup>, Algirdas Selskis<sup>1</sup>, Rimantas Ramanauskas<sup>1</sup>

<sup>1</sup>State research institute Center for Physical Sciences and Technology, Savanorių ave. 231, LT-02300 Vilnius, Lithuania  
aliona.kirdeikiene@ftmc.lt

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## INTRODUCTION

Ce based coatings can be considered as environmentally friendly alternative to Cr(VI) conversion coatings. Phosphating is one of the most widely used passivation treatments of metals and is one of the promising methods for enhancing the corrosion resistance of steel. Formation of this conversion coating occurs via the growth and coalescence of phosphate crystals, what inevitably leaves pores, which reduces corrosion resistance. The protective ability of phosphate coatings on steel could be improved by the passive layer modification with Mo compounds. Conversion coatings of Ce compounds, forming a physical barrier on the metal surface, insulate it from the environment and are therefore considered to be the most environmentally friendly method to modify the metal surface. In addition, Ce oxide coatings provide self-healing properties. The aim of the present study was to evaluate the protective and self-healing capacities of phosphate/molybdate and cerium-modified phosphate/molybdate conversion coatings on a steel surface and to study the process of a new passive film formation on the artificially damaged areas of these coatings.

## EXPERIMENTAL

Phosphate-molybdate (Fe/P-Mo) and phosphate-molybdate-cerium (Fe/P-Mo-Ce) coatings were deposited on steel surface. The solution used for the Fe/P-Mo chemical conversion treatment contained: 0.15 M H<sub>3</sub>PO<sub>4</sub>, 0.003 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, 0.1 M Na<sub>2</sub>MoO<sub>4</sub> and 0.02 M NaNO<sub>3</sub>, pH ~ 4.5, 50 °C. Ce-modified conversion coatings were deposited by simple immersion of Fe/P-Mo samples into one of two solutions (pH ~ 5, 25 °C) containing 0.05 M Ce(NO<sub>3</sub>)<sub>3</sub> (Fe/P-Mo-Ce1) or 0.05 M Ce(NO<sub>3</sub>)<sub>3</sub> + 0.025 M Na<sub>2</sub>SO<sub>4</sub> (Fe/P-Mo-Ce2).

Different surface analytic techniques, including FIB-SEM, TEM and XPS, together with electrochemical measurements (EIS) were applied in order to obtain complementary information of this coating system.

## RESULTS

### CORROSION BEHAVIOR

#### Protective ability

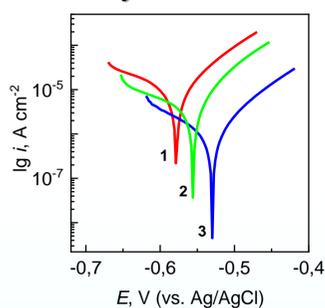


Fig. 1. Potentiodynamic polarization curves of the conversion coating electrodes: 1 – Fe/P-Mo; 2 – Fe/P-Mo-Ce1; 3 – Fe/P-Mo-Ce2 in a 0.5 M NaCl solution at 25 °C; potential scan rate 0.5 mV s<sup>-1</sup>.

#### Electrochemical parameters

Table 1. The electrochemical parameters and protection efficiency (P%) of conversion coatings determined in 0.5 M NaCl solution.

Sample	Electrochemical parameters		
	E <sub>corr</sub> V (vs Ag/AgCl)	i <sub>corr</sub> A·cm <sup>-2</sup>	P %
Fe/P-Mo	-0.569	2.2 · 10 <sup>-6</sup>	50
Fe/P-Mo-Ce1	-0.515	1.7 · 10 <sup>-6</sup>	68
Fe/P-Mo-Ce2	-0.490	2.7 · 10 <sup>-7</sup>	95

#### Self-healing ability

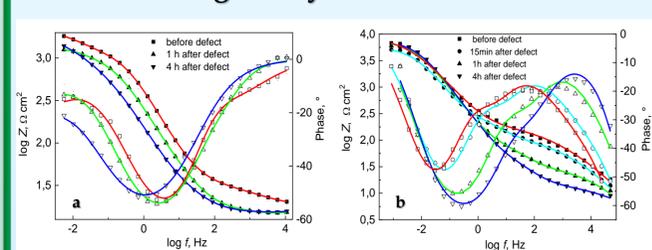


Fig. 2. Impedance spectra of Fe/P-Mo (a) and Fe/P-Mo-Ce (b) in 0.5 M NaCl solution before and after sample scratching.

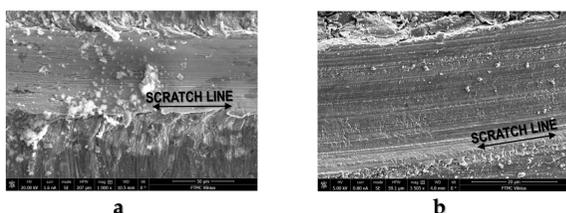


Fig. 3. SEM images of scratches on Fe/P-Mo-Ce1 (a) and Fe/P-Mo-Ce2 (b) coatings after immersion in 0.5 M NaCl solution. Exposure time: a – 2 h; b – 4 h.

### MORPHOLOGY AND INNER STRUCTURE

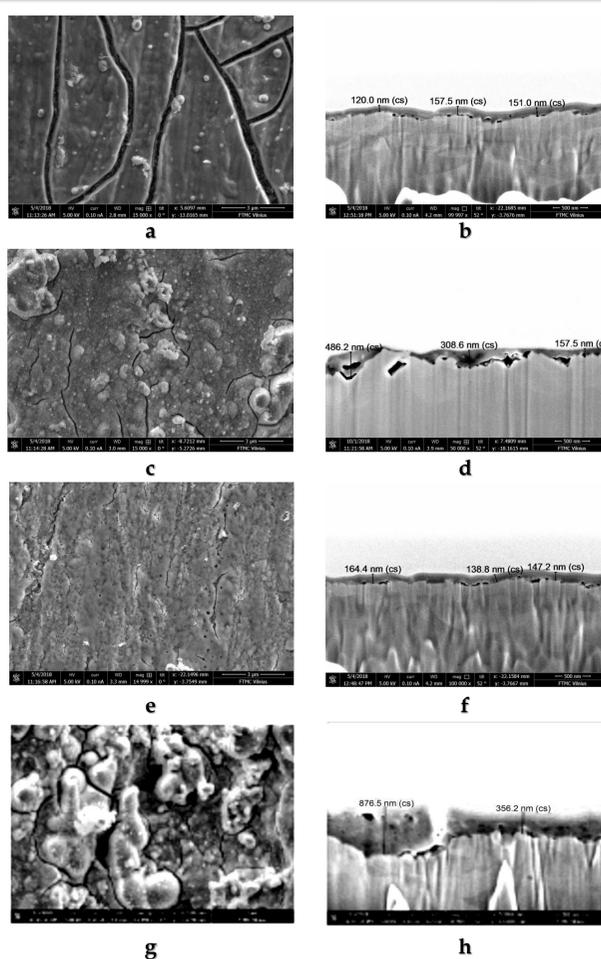


Fig. 4. Top (a, c, e, g) and cross-sectional (b, d, f, h) focused ion beam scanning electron microscope (FIB-SEM) images of Fe/P-Mo (a, b), Fe/P-Mo-Ce1 (c, d, g, h) and Fe/P-Mo-Ce2 (e, f) conversion coatings. Conversion layer deposition process duration: Mo (a–h) – 20 min, Ce (c–f) – 20 min, (g, h) – 40 min.

#### Chemical composition

Table 2. Composition of the conversion coatings (energy dispersive X-ray (EDX) results for samples prepared for SEM analysis).

Sample	Element concentration (atomic %)					
	Fe	O	P	Mo	Ce	S
Fe/P-Mo	67.39	29.48	1.34	1.79	-	-
Fe/P-Mo-Ce1	50.17	44.99	1.45	1.39	1.75	-
Fe/P-Mo-Ce2	57.67	37.74	1.58	1.22	2.24	0.22

### RESULTS OF SURFACE ANALYSIS

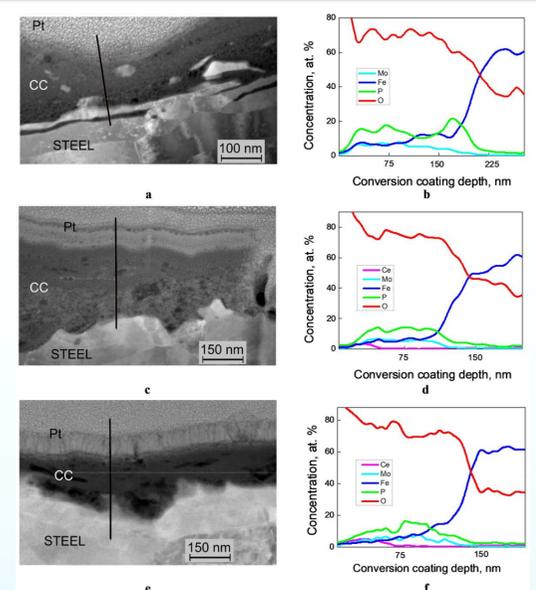


Fig. 5. Cross-sectional TEM images (a, c, e) and element concentration profiles (b, d, f) of Fe/P-Mo (a, b), Fe/P-Mo-Ce1 (c, d) and Fe/P-Mo-Ce2 (e, f) conversion coatings.

#### XPS spectra

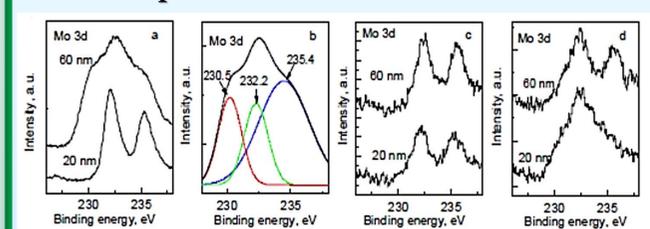


Fig. 6. XPS spectra of Mo 3d for Fe/P-Mo (a, b), Fe/P-Mo-Ce1 (c) and Fe/P-Mo-Ce2 (d) coatings at 20 and 60 nm depth. (b) Deconvolution of Mo 3d peak of Fe/P-Mo sample at 60 nm depth.

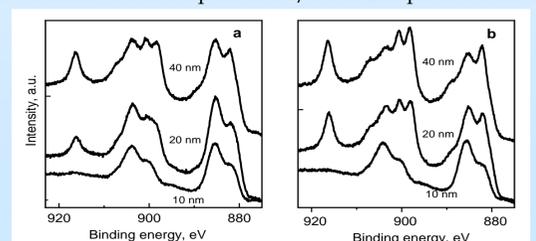


Fig. 7. X-ray photoelectron spectroscopy (XPS) spectra of Ce 3d for Fe/P-Mo-Ce1 (a) and Fe/P-Mo-Ce2 (b) samples after Ar sputtering for different times.

## CONCLUSIONS

The protective corrosion properties of the investigated conversion coatings depend on their morphology, microstructure and composition. The increase in the deposition process time of the molybdate and cerium layer is significant for the increase in the number of structural defects. The presence of sulphate ions in the Ce solution favored the formation of a thinner conversion layer, which had a significantly lower number of structural defects and had the best protective properties among all the investigated coatings. Modification of phosphate/molybdate coatings with Ce ions resulted the conversion layer was supplemented with a mixture of Ce (III) and Ce (IV) oxides present in the outer part of the coating, which determined their self-healing possibilities. This can be explained both by the larger fraction of Ce (IV) in the conversion coating and the lower number of structural defects.