



Corrosion rates of green novel hybrid conversion coating on aluminium 6061

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ARTICLE INFO

Keywords:

Hybrid conversion coating
Corrosion performance
Sabdariffa calyx
Aluminium
Polarization

ABSTRACT

The use of chromate conversion coatings have been limited by several protocols as a result of their carcinogenicity and toxicity towards humans and the environment. Searches are ongoing for chromate replacement in coating baths and processes. This paper describes the comparison among the corrosion rates of a novel hybrid conversion coating derived from water extracts of *hibiscus sabdariffa calyx* in conjunction with ammonium molybdate, a molybdate conversion coating and the so-called chromate conversion coating. Potentiodynamic polarization measurement in 3.5 wt% sodium chloride solution was employed in ranking the coatings as *sabdariffa* molybdate being more corrosion resistant than chromate, which in turn out performed molybdate.

1. Introduction

Corrosion inhibitors are precursor chemicals for the formation of conversion coatings on metals including the so called chromate conversion coatings which have been categorized as carcinogenic and environmental pollutants [1,2]. Compounds with lower toxicity, such as molybdate [3], permanganate [4], vanadate [5] and zirconate [6] as well as zirconate combined with trivalent chromium have been employed in conversion coating formation on light alloys. Most of these have their shortcomings, however, zirconium/trivalent chromium which gained prominence from the 1990s till the present day have been found to contain Cr^{6+} species. It has been suggested to occur through some exchange of electrons to Cr^{3+} from peroxides generated from cathodic reactions on second phase inclusions in the Al matrix [7,8]. Hence, it has become necessary to develop coatings devoid of any chromium specie. However, organic additives have been found to influence the corrosion resistance and improved adhesion characteristics of some hybrid conversion coatings.

2. Methods

Aluminium 6061, donated by First Aluminium Plc, Nigeria, with nominal composition of 96.85% Al, 0.9% Mg, 0.7% Si, 0.6% Fe, 0.3% Cu,

0.25% Cr, 0.20% Zn, 0.10% Ti, 0.05% Mn, and 0.05% others was made out into spade-like electrodes, etched in 10% NaOH, rinsed in water, desmuted in 50% w/w HNO_3 , rinsed in water and dried under the fan for 30 minutes prior to being stored in a desiccator. Conversion coating solutions were prepared in 1 L of water thus: (a) Chromate conversion coating (CCC); 4g/l chromic acid and 1g/l NaF; (b) Molybdate conversion coating (MCC); 4 g/l ammonium molybdate and 1g/l NaF, (c) *Sabdariffa*-molybdate conversion coating (SMCC); 500 g/l of dried *sabdariffa calyx*, allowed to stand for 30 minutes, decanted add 4 g/l ammonium molybdate and 1g/l NaF. All chemicals are of laboratory grade from BDH chemicals, UK. The cleaned electrodes were immersed separately in the conversion coating baths for various times ranging from 30 s to 10 minutes. After each immersion period, they were rinsed in running water and dried over night at room temperature. For potentiodynamic measurements, specimens treated for 3 mins each in the coating baths were mounted in a resin such that, as working electrodes, they have an exposed area of 1.13 cm^2 each. With the use of Digi-Ivy 2300 potentiostat and a three electrode cell comprising of platinum as counter electrode, silver/silver chloride (Ag/AgCl) as reference electrode while the variously conversion coated specimens served as working electrodes. As previously discussed [9], measurements were carried out from -1.5 V to $+1.5$ V at a scan rate 0.0016V/s according to ASTM G102-89 (2015). The measurements were performed at 24 and 72 h of immersion of the

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<https://doi.org/10.1016/j.rineng.2020.100159>

Received 6 June 2020; Received in revised form 28 July 2020; Accepted 29 July 2020

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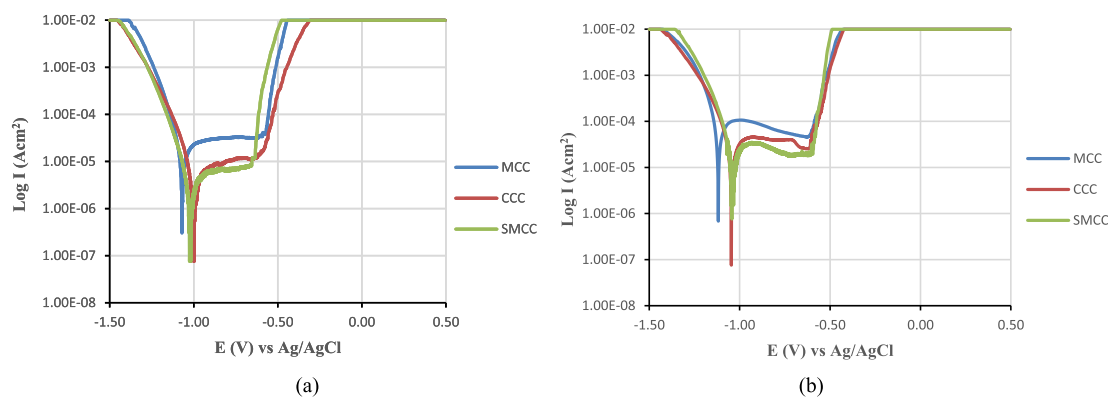


Fig. 1. Polarization curves for conversion coated specimens (a) at 24 h and (b) at 72 h of exposure in 3.5% NaCl.

Table 1

Polarization scans for the conversion coated specimens at 24 h in NaCl solution.

Samples	Corrosion Rate, C_R (mm/y)	Corrosion Current, I (A)	Corrosion Current Density, i_{corr} (A/cm ²)	Corrosion Potential, C_p (V)	Polarization Resistance, R_p (Ω)	Cathodic Tafel Slope, B_c (V/dec)	Anodic Tafel Slope, B_a (V/dec)
MCC	0.089	1.69E-05	8.04E-06	-1.070	1522.00	-11.420	2.566
CCC	0.019	3.55E-06	1.69E-06	-0.997	7229.00	-10.910	2.423
SMCC	0.015	2.94E-06	1.40E-06	-1.017	8726.00	-11.53	3.076

Table 2

Polarization scans for the conversion coated specimens 72 h in NaCl solution.

Samples	Corrosion Rate, C_R (mm/y)	Corrosion Current, I (A)	Corrosion Current Density, i_{corr} (A/cm ²)	Corrosion Potential, C_p (V)	Polarization Resistance, R_p (Ω)	Cathodic Tafel Slope, B_c (V/dec)	Anodic Tafel Slope, B_a (V/dec)
MCC	0.834	7.57E-05	7.57E-05	-1.118	339.40	-10.600	1.493
CCC	0.292	2.66E-05	2.66E-05	-1.046	967.80	-9.748	1.995
SMCC	0.259	2.35E-05	2.35E-05	-1.043	1092.00	-11.46	1.459

various specimens in 150 ml of 3.5% NaCl solution. The corrosion current densities, i_{cor} and the corrosion potential, E_{cor} for the variously conversion coated specimens were calculated from the Tafel plots of log current versus potential.

3. Results and conclusion

The polarization plots for the variously conversion coated Al 6061 in NaCl at 24 and 72 h of exposure are displayed in Fig. 1 (a) and (b) respectively while Tables 1 and 2 present the contemporary results from the respective polarization scans.

The novel hybrid conversion coating, SMCC showed superior corrosion resistance in NaCl with corrosion current densities of 1.40×10^{-6} at 24 h and 2.35×10^{-5} A/cm² at 72 h as against those of CCC with corresponding 1.69×10^{-6} and 2.66×10^{-5} A/cm² respectively. The least corrosion resistance was displayed by MCC with corrosion rates of 8.04×10^{-6} and 7.57×10^{-5} A/cm² at 24 h and 72 h respectively in NaCl solution.

Coatings developed from traditional chromate coating baths are usually characterized with mud-cracking morphology [10] which constitutes flaws through which aggressive ions such as chlorides can initiate pitting corrosion of the substrate aluminium. However, when the coating bath is modified with OH⁻ (hydroxyl) containing organic compounds, such cracks which may penetrate to the substrate/coating interphase are usually obliterated and the coating made more compact [11,12]. In addition, according to Gao et al. [13], hydroxyl groups attract chelated metal-organic complexes. Such are formed in hybrid organic/inorganic conversion coatings. These, readily promote the diffusion of the metal complexes affording a higher reaction rate for the metal ion, which may be any highly oxidizing metal ion in solution. Thus, SMCC with chelated Mo (VI) complex will diffuse relatively faster than Cr (VI) to stifle

corrosion reactions on the substrate aluminium. Hence to all intents and purposes, SMCC out performed CCC as revealed in the PDP corrosion measurements. However, Saji [14] in his review demonstrated that MCC is unattractive as a corrosion limiting coating on aluminium because of its low oxidizing capacity as compared to CCC.

In conclusion, the rating of the coatings in terms of corrosion performance is *Sabdariffa* molybdate (SMCC) > Chromate (CCC) > Molybdate (MCC). However, research is ongoing to further characterize the coatings with SEM/EDS, FTIR, XPS etc.

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.

Acknowledgements

Authors appreciate the Landmark University Centre for Research, Innovation and Development (LUCRID) through the group Innovation, Industry and Infrastructure.

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