European Journal of Sustainable Development (2019), **8**, 5, 9-15 ISSN: 2239-5938
Doi: 10.14207/ejsd.2019.v8n5p9

Use of Industrial Waste to Produce Ceramic Coatings on Metal

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Abstract
Industrial processes are activities that produce large amounts of wastes. Often these wastes are disposed in dam or landfills, occupying large areas and causing environmental damage such as the contamination of water and soil. According to the Circular Economy concept, waste should be minimized and reused as raw material in a new process. This work describes two residues, namely red mud (bauxite residue) and waste foundry sand (WFS), whose chemical compositions indicate their suitability for use as protective coatings. These residues were used to obtain coatings on aluminum alloy by employing plasma electrolytic oxidation (PEO). The PEO process enables the creation of coatings that are durable, uniform, and strongly adherent on metallic components of different shapes. The mineralogical compositions of the coatings were investigated using X-ray diffraction (XRD). Surface wettability was determined by contact angle measurements and evaluation was made of the average surface roughness. Alumina was the main phase observed by XR, indicating good chemical stability and high thermal resistance. The coatings obtained with the red mud were thicker and less rough, compared to those obtained with the WFS. The results demonstrated the feasibility of using these wastes for coating metals in order to improve their properties and enable new applications.

Keywords: Industrial Waste, Red Mud, Waste Foundry Sand, Circular Economy, Ceramic Coating.

1. Introduction

Industrial and mining activities are important for the economies of countries. However, they frequently involve the generation of waste, which can increase costs and constitutes an environmental liability. According to the Circular Economy concept (Pieroni *et al.* 2019, Cong *et al.* 2019), the waste generated by an industry should be used as a raw material in the same production process, or be used by other industries. Therefore, it has become increasingly important to add value to waste, enabling it to be used rather than be discharged into lagoons or sent to landfill. The present work highlights two wastes that are generated in Brazil: red mud (RM) and waste foundry sand (WFS). These wastes are produced in large quantities in different regions of the country and have rich chemical compositions.

Red mud is a highly alkaline residue generated in the Bayer process used for the refining of bauxite in order to obtain alumina and subsequently produce aluminum. It can contain oxides of iron, silicon, titanium, sodium, and aluminum, among others (Antunes *et al.* 2012). In Brazil, it is discharged into lagoons, which have limited storage capacity, occupy extensive areas, and require constant monitoring in order to avoid accidents.

Waste foundry sand is generated by the metallurgical industry during the process of casting of metal items, which requires sand molds into which the liquid metal is poured.

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Fine particles are produced during preparation of the molds, as well as during demolding, which are collected by the exhaust system and are discarded as waste. Since this sand is composed mainly of silicon, it is usually classified as non-hazardous and inert waste and is disposed of in industrial landfills, which significantly adds to the cost of the industrial activity (Siddique, 2014).

Both red mud and WFS have applications in civil construction (Evans, 2016, Gurumoorthy and Arunachalam, 2019) and as adsorbents and catalysts (Evans, 2016, Basal *et al.* 2019). They also have potential for use as coatings on metal surfaces (Antunes *et al.* 2014, Lokesh *et al.* 2018).

The coating of metallic surfaces with layers of ceramic material is a simple way to extend the useful lifetimes of products, protecting them against environmental factors that lead to corrosion and wear (Callister, 2007). One of the techniques used to obtain such protective coatings on metals is plasma electrolytic oxidation (PEO) (Yerokhin *et al.* 1999). This technique is similar to anodizing, but involves the use of higher voltages, with the formation of micro-arcs due to the effect of the plasma in an electrolytic cell. The advantage of this technique is that it can produce strongly adherent and chemically stable coatings on different shapes and sizes of metal surfaces (Clyne *et al.* 2019). It has been shown that these ceramic coatings can be produced on materials such as aluminum alloys, titanium, and carbon steel, among others (Lu *et al.* 2016), using these substrates in an electrolytic solution, hence providing them with new properties and applications. Recent studies have shown that it is possible to incorporate silicon-rich wastes in the electrolytic solution, resulting in the formation of good quality ceramic coatings on aluminum (Sottovia *et al.* 2014, Souza *et al.* 2019).

This work compares the coatings obtained using red mud and WFS at concentrations of 10 g/L in the electrolytic solution. In both cases, the coatings were produced by PEO on aluminum alloy. Evaluation was made of the effects of these two silicon-rich wastes on the characteristics of the coatings, considering their crystallinity, morphology, thickness, and wettability, in order to enable possible applications to be identified.

2. Experimental

2.1 Collection and characterization of the wastes

The red mud used in this work was collected at a bauxite refining plant located in São Paulo State, Brazil. The samples (in the form of paste) were removed from the discharge lagoon and were dried for 48 h at 50 ºC, prior to use in the experiments. The WFS was collected from the exhaust system of a foundry and was used without any prior treatment.

The chemical compositions of these waste samples were determined previously (Souza *et al.* 2019) and are summarized in Table 1. The WFS consisted mainly of silicon oxide, which accounted for over 80% of the mass, followed by aluminum and iron oxides. The red mud also contained these major components, but with predominance of the iron and aluminum oxides.

Table 1. Chemical compositions of the wastes.

	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	CaO	K_2O	TiO_2	MgO
RM (wt%)	19.82	30.53	30.87	8.31	4.74	0.19	2.99	0.98
WFS (wt%)	82.98	9.76	4.22	0.28	0.25	1.46	0.50	0.46

The crystalline structures of the wastes were investigated by X-ray diffraction (XRD) analysis, using a Panalytical X'Pert Pro diffractometer operated at 45 kV and 40 mA, with Cu Kα radiation. The morphologies were observed by scanning electron microscopy (SEM), with the elemental compositions obtained by energy dispersive spectroscopy (EDS/SEM), employing a JEOL JSM-6010LA microscope.

2.2 Preparation and characterization of the aluminum substrates

The coatings were deposited onto substrates of 5052 aluminum alloy (chemical composition: 0.25% Si, 0.40% Fe, 0.10% Cu, 0.10% Mn, 2.8% Mg, 0.15% Cr, 0.10% Zn, and remainder aluminum (data provided by the supplier)) and 1200 aluminum alloy (chemical composition: 98.75% Al, 1% Si, 1% Fe, 0.05% Ti, 0.05% Mn, 0.05% Cu, and 0.1% Zn (data provided by the supplier)), each with thickness of 1.5 mm. The substrates were cut into pieces sized 25 mm x 25 mm and were cleaned and polished, prior to the depositions performed by PEO.

Before coating, wettability (hydrophobic or hydrophilic characteristics) analysis of the aluminum alloy substrates was performed according to the water drop contact angle method, using a goniometer (Model 100-0, Ramè Hart). The surface roughnesses were analyzed using a profilometer (DekTak, Veeco), obtaining the arithmetic mean (Ra) of the deviations from the baseline.

2.3 Use of PEO to produce the ceramic coatings on the alloys

The PEO system used to obtain the coatings consisted of a high voltage source connected to a reactor filled with electrolytic solution containing the waste (Figure 1). The cathode consisted of a curved stainless steel plate, while the anode was the metal substrate to be coated, which was immersed in the solution. A high voltage was supplied from an alternating current source (MAO-30 Power Supply). The depositions using WFS in the electrolytic solution were performed using a voltage of 600 V, while the depositions using red mud employed a voltage of 650 V. Under these conditions, it was possible to observe the appearance of micro-arcs. The frequency used was 200 Hz.

The electrolytic solutions were prepared using concentrations of 10 g of waste in one liter of the solution, with addition of 1 g of potassium hydroxide to adjust the conductivity (when necessary). A deposition time of 900 s was used for both coatings. The coatings obtained with red mud and WFS were denoted RMC and WFSC, respectively.

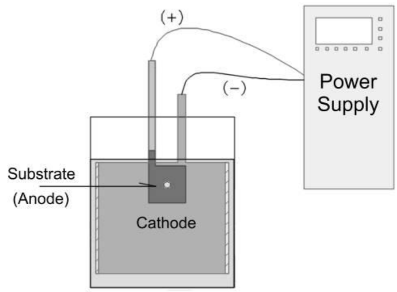

Figure 1. Schematic illustration of the reactor and PEO system.

2.4 Characterization of the ceramic coatings obtained on the aluminum alloys using PEO

The morphologies of the coatings were evaluated by SEM, with micrographs acquired using the JEOL JSM6010LA microscope operated at 25 kV, in secondary electron mode. The energy dispersive spectroscopy (EDS) module coupled to the microscope enabled microanalysis of the elemental compositions of the coatings. The thicknesses of the coatings were determined by the parasitic current method, using a MINIPA MCT-401 probe. The mineralogy of the phases in the coatings was identified by XRD. The hydrophilic/hydrophobic characteristics of the coatings were evaluated by wettability analyses, while the surface roughnesses were determined by profilometry.

3. Results and Discussion

3.1 Characterization of the wastes

The SEM micrograph of the red mud waste (Figure 2) showed that it was composed of particles of different sizes and shapes. The EDS analysis revealed the presence of the elements Al, Si, Fe, Ca, Na, and Ti. The WFS particles (Figure 3) had varied shapes and were larger than the red mud particles. The EDS analysis showed the presence of the same elements found in the red mud, together with Mg and K.

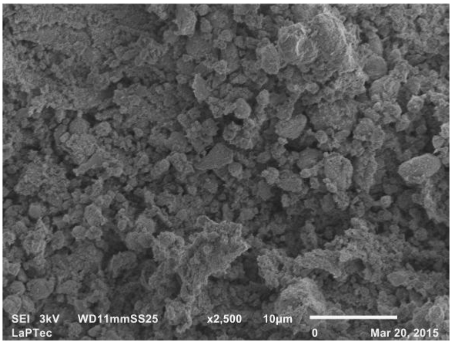

Figure 2. Particle characteristics of the red mud.

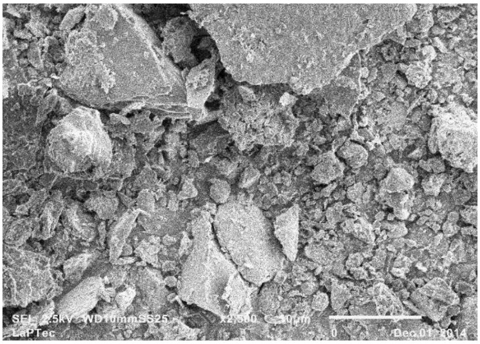

Figure 3. Particle characteristics of the WFS.

The XRD analyses showed that the red mud contained hematite (Fe_2O_3), goethite ($FeO(OH)$), quartz (SiO_2), gibbsite ($Al(OH)_3$), calcite ($CaCO_3$), sodalite, kaolinite, and rutile (TiO_2). The WFS showed peaks corresponding to quartz, hematite, crystalline potassium oxide (K_2O), alumina (Al_2O_3), sodium oxide (Na_2O_2), and periclase (MgO).

3.2 Characterization of the aluminum alloy substrates

Table 2 shows the results of the roughness and contact angle measurements of the aluminum alloys used as substrates for the coatings.

Table 2. Results obtained for the wettability (contact angle) and roughness of the aluminum alloys.

	Al 5052	Al 1200
Ra (µm)	0.38±11	0.136±0.069
Contact angle (°)	70.0±0.1	84.06±0.14

Prior to application of the ceramic coatings, the substrates could be classified as having hydrophilic surfaces, since the contact angles were smaller than 90°. The roughnesses of the two samples were of the same order of magnitude.

3.3 Characterization of the ceramic coatings obtained by PEO on the alloys

Figure 4 shows images of the uncoated aluminum substrate (a) and the substrates with coatings obtained using red mud (b) and WFS (c). It can be seen that compared to the metal surface, the coatings had a more matt appearance, with a light grey coloration.

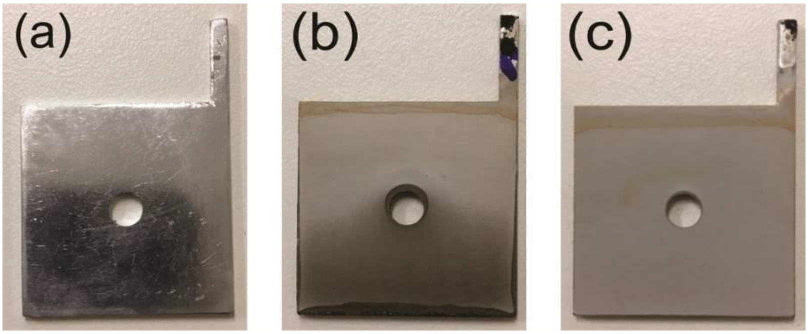

Figure 4. (a) uncoated aluminum substrate. (b) substrates with coatings obtained using red mud. (c) substrates with coatings obtained using WFS.

The morphologies of the coatings, observed using SEM (Figure 5), revealed regions of coalescence and pores, characteristic of ceramic coatings. In the case of the coating obtained using WFS, there was the presence of loose particles above the coalesced material.

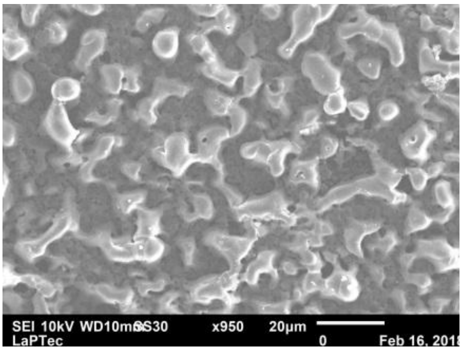

Figure 5(a). SEM micrograph of the surface of the coating obtained using red mud (RMC).

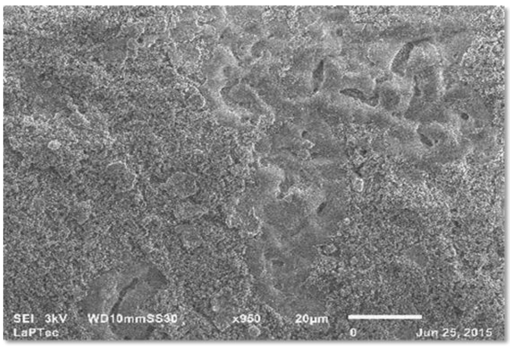

Figure 5(b). SEM micrograph of the surface of the coating obtained using WFS (WFSC).

The EDS analysis showed the presence of Al, Fe, Si, and Ti in the coatings obtained with the red mud, while the coatings obtained with WFS showed the additional presence of Mg, Ca, Na, and K. The magnesium was a component of the 5052 alloy, while the other constituents were from the waste. These results showed that there was a greater variety

of elements in the depositions obtained with the WFS, although the coatings presented weaker adherence, compared to those obtained with the red mud, since there were loose particles present on the surface of the ceramic coating.
The XRD results (Figure 6) showed that the aluminum present in both coatings was in the form of γ-alumina and iron. Differences in crystallinity between the two coatings were related to the presence of periclase (MgO) in the coatings produced with WFS, while the coatings obtained with red mud showed the formation of crystalline Al-Ti structures. The presence of alumina indicated that the coatings were highly thermally and chemically stable.

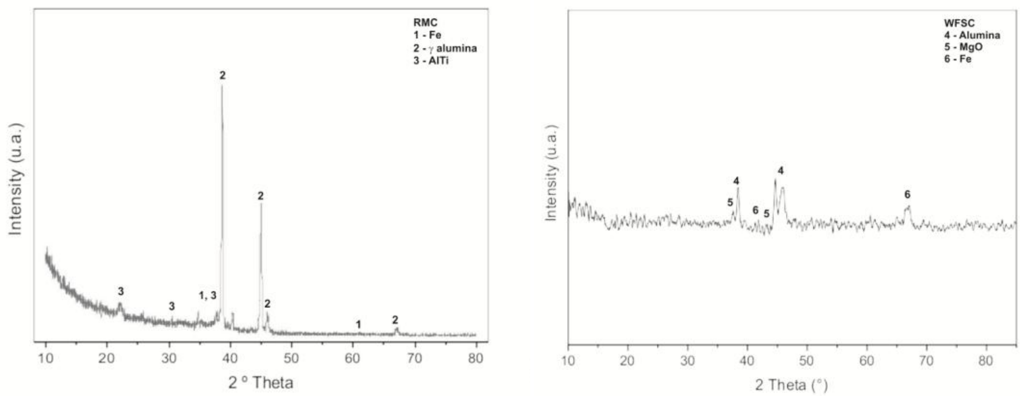

Figure 6. Results of XRD analyses of the samples: RMC – red mud coating, WFSC – WFS coating.

The results obtained for the thickness, roughness, and contact angle of the coatings are shown in Table 3.

Table 3. Evaluation of the thickness, roughness, and wettability (contact angle) of the coatings obtained with the wastes.

	RMC	WFSC
Thickness (μm)	12.4±2.8	7.01±0.34
Ra (μm)	2.77±1.46	5.47±3.6
Contact angle (°)	107.13±0.94	83.04±1.91

The SEM images showed that the coatings obtained using the red mud were thicker and less rough, compared to those produced with the WFS, suggesting that the former might be more resistant to mechanical wear. Coating using the red mud altered the wettability of the surface of the aluminum substrate, since the ceramic layer caused it to become hydrophobic, instead of hydrophilic.

4. Conclusions

The SEM/EDS analyses showed that the coatings obtained using the WFS contained a greater variety of chemical elements, but adhered less strongly to the metal surface, compared to the coatings obtained using the red mud.

Both coatings could be characterized as ceramic materials containing alumina, which is thermally and chemically stable, indicating that they could be used under demanding conditions.

The coatings obtained using the red mud were thicker and less rough, compared to the coatings obtained with WFS, suggesting that they should be more resistant to mechanical wear and more suitable for use under conditions where the metal is liable to substantial physical attrition. Furthermore, the coating obtained with the red mud provided a hydrophobic surface that could prevent contact of the substrate with water, hence minimizing the possibility of corrosion.

5. Acknowledgments

The authors would like to thank CAPES for financial support.

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