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Application of Yttrium Oxide Nanoparticles Produced by the Pechini Method on the Surface of Grey Cast Iron as a Protective Method Against High Temperature Oxidation

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Extended Abstract

Metallic materials, when exposed to high temperatures, are subject to a corrosive process called oxidation, that may affect the structural integrity of the material causing failures. The use of rare earth elements, such as yttrium, in alloys has been widely studied to protect materials against oxidation, but the application of these elements as oxides on the metallic surface might offer the same protective behavior. Considering this, yttrium oxide nanoparticles were produced by the Pechini method and applied on grey cast iron using an ethanol suspension. The corrosion protection was evaluated by mass gain test, exposing to 600 °C for a period of 10 h. The results were then adjusted to the kinetic parabolic law to obtain the corrosion rate. The presence of yttrium oxide reduced the oxidation kinetics of the material indicating that the use of the oxide can be a potential solution to protect grey cast iron against oxidation.
Keywords: Rare Earths, Coating, Corrosion

1 Introduction

Cast irons are widely used in engineering, due to their good characteristics related to availability, properties, recyclability and low cost[1,2]. These materials are often exposed to high temperatures environments, being subject to high temperature oxidation[2]. In this process, an oxide scale is formed and controls the continuation of the oxidation. A dense and adherent scale is desired to promote the best protection for the material[3]. The addition of alloying rare earth elements is one of the ways to protect materials against oxidation, due to the reactive-element effect [3,4]. The same effect can be obtained by a rare earth oxide coating on the surface of the material to be protected, and reducing the oxide particle size can increase its protective effect, so nanoparticles can present the best results[5]. Among the rare earths, yttrium is considered the best options, due to its availability and high efficiency in the protection against high temperature oxidation [5, 6]. The Pechini method stands out as a way to produce yttrium oxide nanoparticles due to its relative low cost, possibility of large-scale production and control of the morphology of the formed oxide. This method consists in the formation of a polymer chain where the desired cation is complexed and immobilized to the polymer structure followed by a calcination to eliminate the organic part and form the oxide [7]. Thus, the objective of this study was to produce yttrium oxide nanoparticles by the Pechini method and evaluate its protection against high temperature oxidation of GG25 grey cast iron.

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2 Methodology

Yttrium oxide powder was prepared using the Pechini method. Citric acid (CA) and yttrium (III) nitrate hexahydrate were added to distilled water, agitated until complete dissolution and heated to 50 °C. Then, ethylene glycol (EG) was added to the solution and the temperature was increased to 100 °C to remove the excess water. The system was then heated to 150 °C under constant agitation for 1 hour to form the resin. The molar proportions of the used reagents were AC:EG – 6:4 and Y^{3+}:AC – 0,1:10. The resin was heat treated at 220 °C for 5 hours to expand and remove the excess ethylene and calcinated at different temperatures (600 °C and 800 °C) for 4 hours. The oxides produced were characterized morphologically and structurally by Scanning Electron Microscopy (SEM) and X-Ray Diffractometry (XRD).

A dispersion of yttrium oxide nanoparticles in ethanol was prepared and pulverized on the surface of GG25 grey cast iron. The covered metallic plates were then exposed to 600 °C for 10 hours, removing a sample every 2 hours and measuring the mass variation. The obtained curves were then fitted to the parabolic oxidation law to obtain the oxidation rate of the system, according to equation $(\Delta m/S)^2 = 2k_p t$, where m is the mass, S is the surface area, k_p is the kinetic constant for the parabolic law and t is the oxidation time.

3 Results

SEM micrographs and XRD diffractograms for the produced oxides are presented in Figure 1.

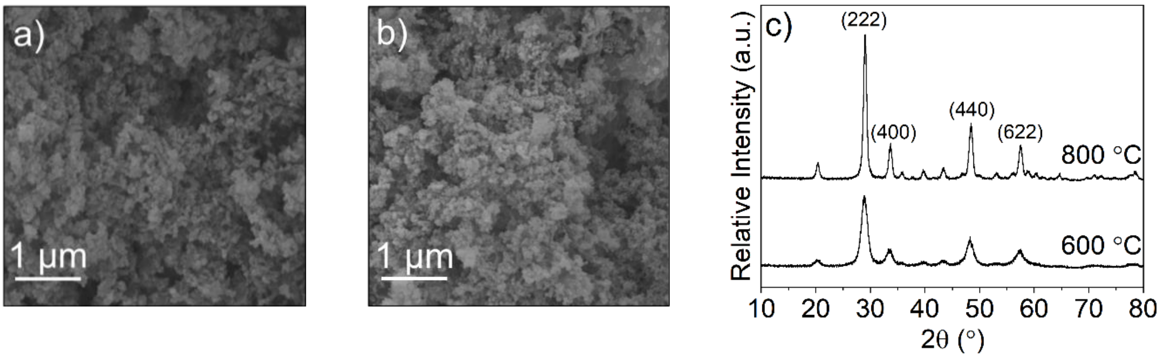

Figure 1 - Morphological and structural characterization of the prepared oxides: a) SEM micrograph 600 °C, b) SEM micrograph 800 °C and c) diffractograms

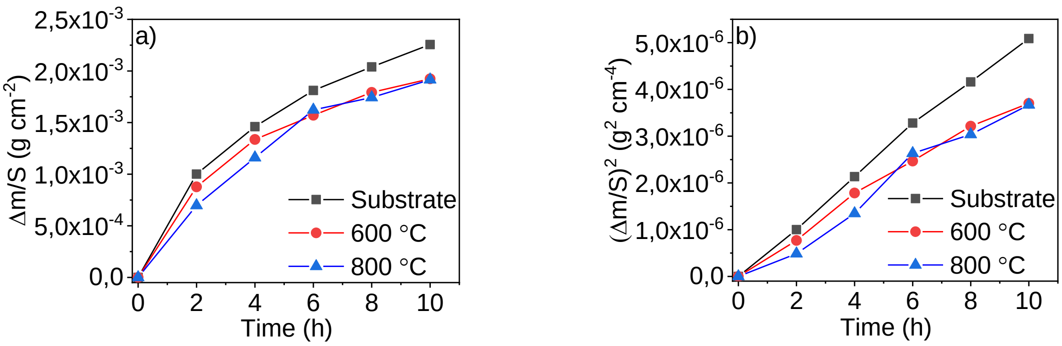

Figure 2 - Mass gain curves: a) mass variation per area unit versus time and b) mass variation per area unit squared versus time

Table 1 – Fitted oxidation kinetic constants

Sample	k_p ($g^2\ cm^{-4}\ s^{-1}$)
Substrate	$7{,}22 \times 10^{-11} \pm 9{,}76 \times 10^{-12}$
600 °C	$5{,}44 \times 10^{-11} \pm 1{,}92 \times 10^{-12}$
800 °C	$5{,}25 \times 10^{-11} \pm 8{,}87 \times 10^{-12}$

Spheroidal nanometric agglomerates were obtained by the Pechini method, with particle sizes of 47,93 ± 0,98 nm and 52,89 ± 1,14 nm for the samples calcinated at 600 °C and 800 °C respectively. The increase in calcination temperature resulted in larger particles sizes, that can be explained by the increase the crystallization kinetics of the material. The peaks observed in the diffractograms for both conditions were indexed to cubic Y_2O_3, according to Powder Diffraction File 83-927. More intense and narrower peaks were observed with a higher calcination temperature, indicating an increase in crystallinity. This can also be explained by the increase of the crystal growth kinetics[8].

Isothermal mass gain test results are depicted in Figure 2 and calculated parabolic kinetic constant values are presented in Table 1. The shape of the curve in Figure 2 (a) and its linearization in Figure 2 (b) can be correlated to the parabolic oxidation kinetic law. With the addition of Y_2O_3 nanoparticles, the curves were dislocated the regions of lower mass gain, indicating the protection of the material against high temperature oxidation. Little difference was observed between the plates coated with the oxides calcinated at 600 °C and 800 °C, suggesting that the small variation in particle size between the samples did not affect the protection against oxidation The curves were then fitted to the parabolic oxidation law equation. A 25% reduction in the oxidation kinetic constants was verified for the samples deposited with Y_2O_3 when compared to the substrate, indicating a reduction in the reaction speed, confirming the protection of the material against high temperature oxidation. Although, due to the quadratic characteristic of the parabolic kinetic constant, this reduction does not reflect the percentual decrease in mass gain for the samples.

The protection promoted by the oxide can be attributed to yttrium's ability to segregate to grain boundary regions. Causing three main effects: the inversion of the main oxide scale growth mechanism, decreasing the oxidation rate, the refining of grain boundaries, increasing scale integrity and the selective oxidation of element such as Al and Cr, present in the alloy, that form protective Al_2O_3 and Cr_2O_3 scales[4].

4 Conclusion

Y_2O_3 nanoparticles were produced by the Pechini method, obtaining particle sizes of 47,93 ± 0,98 nm and 52,89 ± 1,14 nm for the samples calcinated at 600 °C and 800 °C respectively. Mass gain tests curves indicated protection against high temperature oxidation by the deposition of the nanoparticles in the surface of GG25 grey cast iron, with no significative difference between the studied conditions. A reduction of 25% in the parabolic kinetic constant was observed for the coated samples when compared to the bare subtract, confirming the protection of the GG25 grey cast iron by the surface application of Y_2O_3 nanoparticles.

5 Bibliographical references

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