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Thermogravimetric study of 316L steel coated by physical deposit in vapor deposition phase (PVD)

Estudio termogravimétrico de acero 316L recubierto por deposito físico en fase vapor (PVD)

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Abstract

Catastrophic carburization (metal dusting) is one of the problems with the greatest impact on the petrochemical and direct iron reduction industry. This work shows the synthesis of chromium oxide (Cr2O3) coatings on 316L steel as a protective layer to prevent and/or delay material degradation. In this work, the Physical Vapor Deposition (PVD) method will be used, since it is a technique that allows the control of the atmosphere in which the deposition is being carried out, forming high quality thin films, with excellent adherence to the substrate, thus improving its surface properties. Thin films with thicknesses less than one micrometer were obtained, which were subjected to corrosion tests by thermogravimetry in an atmosphere of CH4 at 800°C for 15 minutes and 20 hours, scanning electron microscopy and elemental quantification. The coatings obtained showed an improvement in their resistance to corrosion in critical atmospheric conditions according to the graphs obtained in the thermogravimetry test, observing a lower weight gain compared to the uncoated sample.

Catastrophic carburization, Reduction, Deposition

Resumen

La carburización catastrófica (metal dusting) es una de las problemáticas con mayor repercusión en la industria petroquímica y de reducción directa de hierro. El presente trabajo muestra la síntesis de recubrimientos de óxido de cromo (Cr2O3) sobre acero 316L como capa protectora para prevenir y/o demorar la degradación del material. En este trabajo se empleará el método de Deposición Física de Vapor (PVD), ya que es una técnica que permite el control de la atmosfera en la cual se está realizando la deposición, formando películas delgadas de alta calidad, con una excelente adherencia al sustrato, mejorando así sus propiedades superficiales. Se obtuvieron películas delgadas de espesores inferiores a un micrómetro, que fueron sometidas a pruebas de corrosión por termogravimetría en una atmosfera de CH4 a 800°C por tiempos de 15 minutos y 20 horas, microscopia electrónica de barrido y cuantificación elemental. Los recubrimientos obtenidos presentaron una mejora en su resistencia a la corrosión en condiciones atmosféricas críticas de acuerdo con los gráficos obtenidos en la prueba de termogravimetría observando una ganancia en peso menor en comparación con la muestra no recubierta.

Carburización catastrófica, Reducción, Depósito

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Introduction

Corrosion is the deterioration of a substance or its properties due to reaction with its environment; If the environment is at high temperatures, the phenomenon is called catastrophic carburization (metal dusting). When in contact with highly carburizing atmospheres, vulnerable metals begin a disintegration process generating carbon that will supersaturate the surface when dissolved in the metallic phase, this will cause the destruction of the material by eroding it, mainly affecting the performance of the material in the chemical industries, electrical, energy and transportation (Grabke, 2003).

One of the solutions that have been proposed to delay catastrophic carburization (metal dusting) is to perform a coating using the physical vapor deposition (PVD) technique, this will help preserve and extend the useful life of the materials. One of the candidates with the greatest potential to be deposited is chromium oxide (Cr_2O_3) due to its protective properties against corrosion.

The chrome oxide coating acts as a protective layer, improving the resistance to corrosion of the steel as it modifies the properties of the surface. Some steels such as stainless steels (especially austenitic stainless steels (Y. L. G, 1990)) present this element in their composition, showing resistance to corrosion by themselves because they tend to form a passive oxide layer (T Michler, 2016).

Physical Vapor Deposition Method (PVD)

Being one of the techniques that does not generate contaminants, physical vapor deposition (PVD) is used to transfer material from an atomic level through evaporation, which will later condense on the surface of the substrate, thus forming a thin film (A. V. Rane, 2018) (Ghader Faraji, 2018). This process is carried out in a controlled atmosphere where an inert gas is used to transport the evaporated ions; smooth surfaces with good adhesion, excellent tribological and mechanical properties are produced (Makhlouf, 2011).

The use of the physical vapor deposition (PVD) technique allows deposits of elements, alloys or compounds free of contamination, with good quality and increased adhesion (Baptista, Silva, Porteiro, Míguez, & Pinto, 2018).

Metal dusting

The degradation of both alloys and metals due to the presence of carbon in the environment is known as carburization, this type of corrosion causes failures in different industrial components (D. J. Young, 2011). A consequence of the formation of metallic powders on surfaces is the severe loss of material. At elevated temperatures between 400-700°C carbon dioxide (CO) acts as a reducing gas releasing carbon destroying alloys at an exuberant rate compared to oxygen (Zhang, 2012).

Thin Film Cr/Cr_2O_3

Chromium oxide has high hardness, which allows it to have high resistance to wear, obtaining a low coefficient of friction. These characteristics make it a potential candidate for coating parts or components that are exposed to critical environmental conditions. In the final phase, chrome oxidation changes the microstructure of the surface, increasing the properties of the material on which it is deposited (Laura Dimate Castellanos, 2017).

Methodology

Through roughing and polishing, 316L steel samples were prepared to be processed with the physical vapor deposition technique. Chromium oxide was synthesized on the substrates using a chromium blank and constant oxygen flow. A 20-minute ion wash is performed before adding the pure chrome bond coat for 5 minutes. Once the oxygen is added, the process lasts 30 minutes. The samples obtained are characterized by thermogravimetry (TGA) at different times: 0 and 15 min. and 20 hours; Finally, the characterization was carried out by scanning electron microscopy and an analysis of energy dispersion and mapping by elements.

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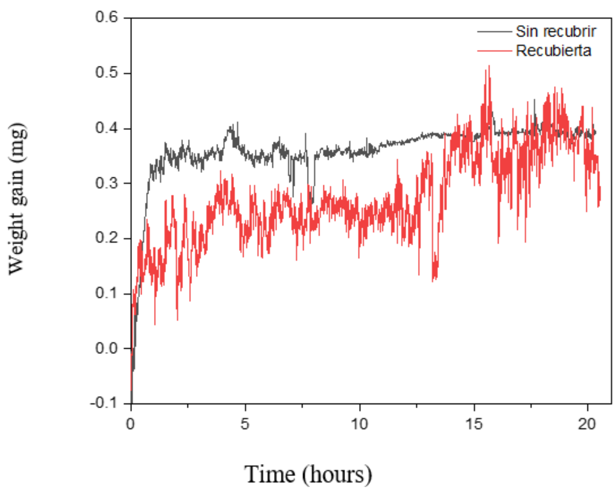
Results and discussion

Thermogravimetry tests were performed at 15 minutes and 20 hours without coating, then a 20-hour test with Cr/Cr_2O_3 coating; Figure 1 shows the graph obtained when performing the thermogravimetry test, the comparison of the samples exposed to corrosion for 20 hours with and without coating is presented.

It can be seen that the coated sample has a lower weight gain compared to the uncoated sample; At approximately 14 hours, both samples show a very close weight gain between both cases, however, in the case of the coated one it is slightly lower.



Graphic 1 Comparative TGA of samples subjected to corrosion for 20 hours

Figure 1 presents the images obtained by scanning electron microscopy, showing the surface of the uncoated 316L substrate, and treated by thermogravimetry at different times. The oxide formation process is observed; before being subjected to corrosion tests, 0 minutes (figure 1a) there is little presence of oxides compared to the sample that was processed for 15 minutes (figure 1b), in which the oxides are more noticeable and begin to form agglomerations; the 20-hour sample (figure 1c), which in the thermogravimetry graph shows an increase in mass, demonstrating that this is due to the formation of oxide on its surface; the figure shows grain boundaries and oxide deposits.

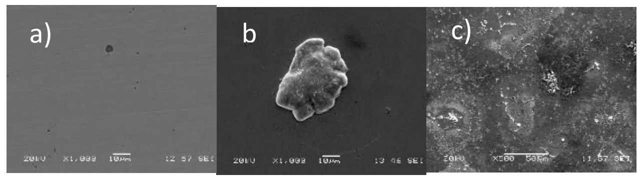


Figure 2 Uncoated 316L steel characterized by thermogravimetry: a) 0 minutes, b) 15 minutes and c) 20 hours

Figure 2 shows the surface of the Cr/Cr_2O_3 coating that was deposited on a 316L steel and subsequently subjected to a 20-hour corrosion test by thermogravimetry. The coating showed a decrease in the formation of oxides; image 3a was obtained by scanning secondary electrons, bright regions were observed so a scan with backscattered electrons was performed (figure 2b) to make these formations visible by atomic contrast.

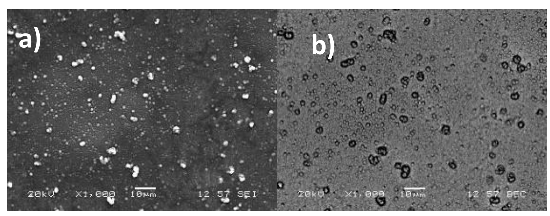


Figure 2 Chromium/chromium oxide coating on a 316L steel characterized by thermogravimetry for 20 hours

Figures 3, 4 and 5 show the element identification analyzes for each of the samples processed by thermogravimetry at 0, 15 minutes and 20 hours that were not coated. Figure 4c shows the amount of chromium present in the substrate while figure 3b gives the amount of oxygen present in the sample.

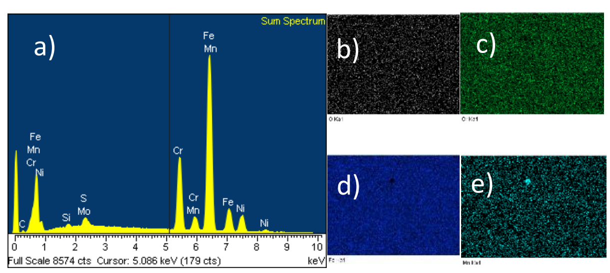


Figure 3 Elemental analysis of uncoated 316L sample with minutes in thermogravimetry. a) Mapping of oxygen in the sample, b) Mapping of chromium in the sample, c) Mapping of iron in the sample and d) Mapping of manganese in the sample

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The region presented in figure 4 has a small accumulation of oxide, this is observed in figure 4b where it is shown that oxygen is present in this region, in the same way there is the presence of chromium in the sample according to figure 4c.

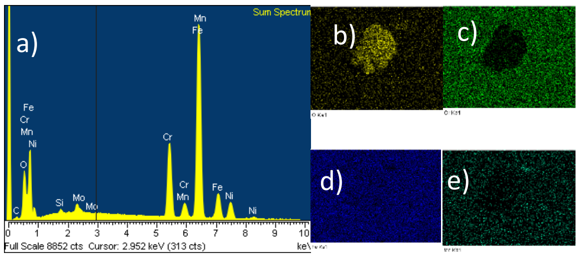

Figure 4 Elemental analysis of the uncoated 316L sample with 15 minutes in thermogravimetry. a) Mapping of oxygen in the sample, b) Mapping of chromium in the sample, c) Mapping of iron in the sample and d) Mapping of manganese in the sample

In figure 5, the analysis by energy dispersion and the mapping by elements of the sample subjected to 20 hours of uncoated corrosion, regions where oxygen (figure 5b) and chromium (figure 5c) are concentrated can be observed, denoting the formation of oxides in these areas.

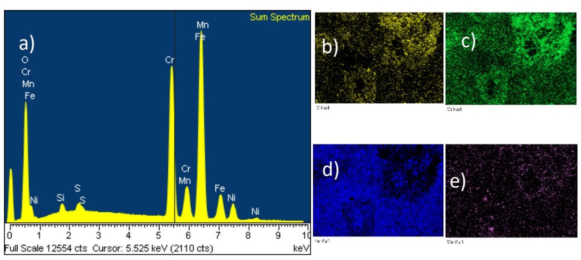

Figure 5 Element analysis of uncoated 316L sample with 20 hours in thermogravimetry. a) Mapping of oxygen in the sample, b) Mapping of chromium in the sample, c) Mapping of iron in the sample and d) Mapping of manganese in the sample

In comparison with the previous images, figure 6 shows the analysis of the sample coated and subjected to corrosion for 20 hours, the energy dispersion analysis shows a higher peak of chromium present in the thin film, it is observed that oxygen figure 6b and the chromium figure 6c are homogeneous throughout the analyzed surface, the iron of the base substrate figure 6d is practically imperceptible due to the layer formed of Cr/Cr_2O_3, this indicates the protective nature of the thin film, which after being subjected to corrosion even is attached to the substrate.

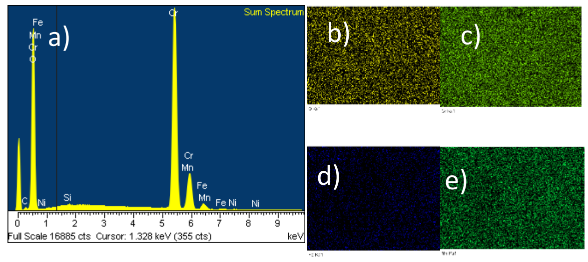

Figure 6 Energy dispersive analysis and element mapping of the 20-hour coated 316L sample in thermogravimetry. a) energy dispersion analysis showing the presence of chromium in the thin film, b) Mapping of chromium in the sample, c) Mapping of iron in the sample and d) Mapping of manganese in the sample

Conclusion

Catastrophic carburization occurs frequently in the industry, so the method of protection by adding thin films on the surface increases the useful life of the material by delaying its degradation.

Cr/Cr_2O_3 coatings created by the PVD process on 316L steel substrates have shown an improvement in resistance to gas corrosion at high temperatures, considerably reducing it.

The results obtained in the present work show that the proposed coating (Cr/Cr_2O_3) generates a protection barrier for the substrate, obtaining a lower weight gain during the thermogravimetry test than the uncoated material, longer corrosion tests are necessary to continue with the study of thin films as corrosion barriers.

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