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TÍTULO PROYECTO : STEEL AS STRUCTURAL MATERIAL FOR HYDROGEN AS ENERGY CARRIER: ANOMALOUS DIFFUSION OF HYDROGEN IN STEEL.

DISCIPLINA PRINCIPAL : INGENIERIA DE MATERIALES
GRUPO DE ESTUDIO : INGENIERIA 1
INVESTIGADOR(A) RESPONSABLE : ALONSO JAQUES SOLIS

DIRECCIÓN :

COMUNA :
CIUDAD : Valparaíso
REGIÓN : V REGION

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INFORME FINAL
PROYECTO FONDECYT INICIACION

OBJETIVOS

Cumplimiento de los Objetivos planteados en la etapa final, o pendientes de cumplir. Recuerde que en esta sección debe referirse a objetivos desarrollados, NO listar actividades desarrolladas.

<table>
<thead>
<tr>
<th>Nº</th>
<th>OBJETIVOS</th>
<th>CUMPLIMIENTO</th>
<th>FUNDAMENTO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Design a set of experiments using electrochemical permeation, with the objective of producing hydrogen diffusion in steel.</td>
<td>TOTAL</td>
<td>The electrochemical permeation set, including potentionstat and electrodes was specified and purchased. The specimen sizing and preparation were defined.</td>
</tr>
<tr>
<td>2</td>
<td>Conduct a series of experiments with electrochemical permeation, designed to verify the occurrence of anomalous diffusion.</td>
<td>TOTAL</td>
<td>A set of experiments involving hydrogen permeation was conducted on steels specimens. The use of Fickian diffusion was insufficient to represent the experimental data thus supporting the use of anomalous diffusion approach.</td>
</tr>
<tr>
<td>3</td>
<td>Analyze the use of fractional calculus in the formulation of anomalous diffusion of hydrogen in steel.</td>
<td>TOTAL</td>
<td>The use of fractional calculus was verified on the experimental measurements of hydrogen permeation. The mathematical solution for diffusion using fractional calculus were implemented in MATLAB and the suitability was verified via regression.</td>
</tr>
<tr>
<td>4</td>
<td>Develop an inverse estimation method for the parameters in fractional diffusion: fractional order and fractional diffusivity.</td>
<td>TOTAL</td>
<td>Analytical and numericals tolos for diffusion modeling using fractional calcules were implemented succesfully. The routines allows the estimation of the parameters and their confidence intervals. This is relevant for determining the suitability of the fractional calculus for this role.</td>
</tr>
<tr>
<td>5</td>
<td>Analyze how the fractional order and fractional diffusivity vary with the density of the grain boundaries</td>
<td>TOTAL</td>
<td>The steel prepared was exposed at different thermal treatment to produce different microstructures with different grain size and grain boundaries densities. The measurements n this experiment setup were no conclusive.</td>
</tr>
<tr>
<td>6</td>
<td>Analyze the role of composition and temperature in fractional diffusion.</td>
<td>TOTAL</td>
<td>The compositionvariation and temperature range worked in the experiments did not allow to have a conclusive model of the temperature variation.</td>
</tr>
</tbody>
</table>

Otro(s) aspecto(s) que Ud. considere importante(s) en la evaluación del cumplimiento de objetivos planteados en la propuesta original o en las modificaciones autorizadas por los Consejos.
RESULTS OBTAINED:
For each specific goal, describe or summarize the results obtained. Relate each one to work already published and/or manuscripts submitted. In the Annex section include additional information deemed pertinent and relevant to the evaluation process.

The maximum length for this section is 5 pages. (Arial or Verdana, font size 10).

RESULTADOS OBTENIDOS:
Para cada uno de los objetivos específicos, describa o resuma los resultados. Relacione las publicaciones y/o manuscritos enviados a publicación con los objetivos específicos. En la sección Anexos incluya información adicional que considere pertinente para efectos de la evaluación.

La extensión máxima de esta sección es de 5 páginas (letra tamaño 10, Arial o Verdana).

Objetivo General

The general goal is to verify that the diffusion process of hydrogen in steels can be represented by a fractional diffusion process.

Objetivos específicos

1.- Design a set of experiments using electrochemical permeation, with the objective of producing hydrogen diffusion in steel.

An experimental setup, consisting in two potentiostat, a permeation cell, electrodes and auxiliary equipment, was designed, purchased and installed. In addition training of the research staff, (PI and assistants) were conducted. The size of the permeation cell were determined to be 250 mL (each container). This these materials and equipment it was possible to implement the ASTM Standard for ASTM G148 - 97(2011) Standard Practice for Evaluation of Hydrogen Uptake, Permeation, and Transport in Metals by an Electrochemical Technique.

The samples sizes and dimensions, made from an High Strength Low Alloy (HSLA) steel were determined. This was critical to obtain samples that are possible to manufacture and being compatible with the experimental cell. Specifically, it was required to overcome sealing problems (between cells), thus reducing the experimental errors and increasing safety. The final size was determined to be coupons of 1 cm x 6 cm. the sample thicknesses are variable and from 0.5 mm to 2.5 mm.

Another variable including in the project is the effect of grain size of the specimens. In order to produce controlled grain size a heat treatment was designed. This objective was part of the presentation “A Fractional Diffusion Interpretation of Hydrogen Permeation in Steel” at 9th International Conference on Diffusion in Solids and Liquids.

2.- Conduct a series of experiments with electrochemical permeation, designed to verify the occurrence of anomalous diffusion.

A series of permeation experiments using the Starkuschi-Devantahn permeations set was conducted as implemented in the ASTM G148 - 97(2011). In order to verify the occurrence of Fickian Diffusion a regression model was fitted to the data and compared with the results observed using a fractional calculus diffusion approach. In order to compare and validate both models a confidence interval analysis was performed. During the analysis is was possible to observe that the permeation curves obtained for steel permeation do not adjust to a Fickian model. However in some cases the deviation from the Fickian diffusion was minimal and it could be represent using traditional diffusion. The observation of anomalous diffusion was confirmed by analyzing the date using the fractional calculus approach. The use of fractional diffusion allows to represent not only anomalous diffusion, also allows for the representation of Fickian diffusion. This objective was part of the presentation “A Fractional Diffusion Interpretation of Hydrogen Permeation in Steel” at 9th International Conference on Diffusion in Solids and Liquids.
3. Analyze the use of fractional calculus in the formulation of anomalous diffusion of hydrogen in steel.

In order to use fractional calculus to analyze the diffusion process it was required to: use this method to represent the mathematically hydrogen permeation in this particular experiment, and to develop and inverse estimation methods. The Fickian mathematical representation of the diffusion process in for this experiment is well known and it is used for diffusivity estimation. Here we develop the mathematical solution for the space fractional case. In addition we work in simplified expression for the fractional diffusion to facilitate the regression process. The developed expression for the Fractional diffusion case is given as a close expression and it can be evaluated using the functions in MATLAB or MS Excel. The determination of the fractional diffusion and fractional diffusion order was developed using regression of the experimental data. To determine both parameters a weighted Non-Linear Least Square regression was implemented. A routing for estimating the confidence interval and uncertainty propagation was determined using montecarlo simulations. This was implemented using MATLAB.

The regression part is done using the optimization routine in MS Excel, SOLVER. In this way it is possible to implement the regression part coupled with the data acquisition. In order to increase the robustness of the estimated for fractional order and fractional diffusion, a stochastic procedure for the regression part was added. This objective was part of the presentation “A Fractional Diffusion Interpretation of Hydrogen Permeation in Steel” at 9th International Conference on Diffusion in Solids and Liquids.

4. Develop an inverse estimation method for the parameters in fractional diffusion: fractional order and fractional diffusivity.

The estimation of the fractional order and fractional diffusion as developed considering different methods. First an analytical solution for the fractional space diffusion was developed. This allows to obtain, for certain boundaries conditions the expected concentration profile. This allows to perform analysis of the fractional diffusivity and fractional order via regression (implemented in MATLAB) using depth profile and concentration profile results. Additionally this allows to obtain the flow vs time on permeation experiments and allows to justify the presence of observed anomalies on those experiments. This could model the cases of experiments no lag was observed or the cases overshooting of the flux vs time.

In addition a numerical model based of finite elements was implemented and used for regression. The advantage of this model is the flexibility in the boundaries conditions. The time fractional part was analyzed considering the analytical solutions available for the system. This objective was part of the presentation “Parameter Estimation in Anomalous Fractional Diffusion Processes”, Materials Science and Technology and the presentation “The Impact of Variable Measurement Spacing in Concentration Profiles Used in Diffusion Experiments” at 10th International Conference on Diffusion in Solids and Liquids – DSL 2014. As part of objective a journal article, describing sampling methods for diffusion experiments, was generated and accepted for publication in the Journal of Phase Equilibria and Diffusion.

5. Analyze how the fractional order and fractional diffusivity vary with the density of the grain boundaries.

In order to produce a variation in the grain boundary density a sample of a High Strength Low Alloy steel, prepared in collaboration with the casting laboratory at the Universidad Michoacana de San Nicolas de Hidalgo. The samples were annealed at 500 C during different times 1, 10 and 100 hours to produce different microstructures. Those samples were analyzed using the electrochemical permeation method described in the standard ASTM G148 - 97(2011). For all the samples analyzed the fractional order resulted to be in the range of alpha=(1,1.5). Therefore suggesting that a superdiffusive process takes place. The variation in the values of alpha due to the thermal treatment were not conclusive to determine how the fractional order varies, and this can be extended to the role of the grain boundaries density.
6.- Analyze the role of composition and temperature in fractional diffusion.

In order to analyze temperature, the room temperature for the experiments was increased. The results do not show a significant evidence in range analyzed. Therefore the current experimental setup was not conclusive regarding to the role of temperature in hydrogen electrochemical permeation. The effect of compositional changes were considered using the steel segregation during solidification. For this range of variation in composition no significant effect was detected in the hydrogen electrochemical permeation.
ARTÍCULOS
Para trabajos en Prensa/ Aceptados/Enviados adjunte copia de carta de aceptación o de recepción.

Nº : 1
Autor (a)(es/as) : Alonso V. Jaques; Ma Belen Barraza; and Jeffrey C. Lacombe
Nombre Completo de la Revista : Journal of Phase Equilibria and Diffusion
Título (Idioma original) : The Impact of Variable Measurement Spacing in Concentration Profiles Used in Diffusion Experiments
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OTRAS PUBLICACIONES / PRODUCTOS

Sin información ingresada.

CONGRESOS

Nº : 1
Autor (a)(es/as) : A. Jaques; Jeffrey LaCombe
Título (Idioma original) : Hydrogen Permeation in Steels via Fractional Diffusion
Nombre del Congreso : Materials Science and Technology
País : CANADA
Ciudad : Montreal
Fecha Inicio : 27/10/2013
Fecha Término : 31/10/2013
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JaquesFractional_Diffusion_MST_20131.pdf

Nº: 2
Autor (a)(es/as): Simpson, R.; Ramírez, F; Nuñez, H.; Jaques, A.
Título (Idioma original): Fractional Calculus a Mathematical Tool ti Improve the Modeling of Mass Transfer Phneomena in Apples
Nombre del Congreso: Annual Meeting Institute of Food Technologists, IFT 2014
País: ESTADOS UNIDOS DE AMERICA
Ciudad: New Orleans
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Nº: 3
Autor (a)(es/as): Simpson, R.; Ramírez, F; Nuñez, H.; Jaques, A.
Título (Idioma original): FRACTIONAL CALCULUS AS A MATHEMATICAL TOOL TO IMPROVE THE MODELING OF MASS TRANSFER PHENOMENA IN APPLES
Nombre del Congreso: 10th International Conference on Diffusion in Solids and Liquids – DSL 2014
País: FRANCIA
Ciudad: Paris
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Autor (a)(es/as) : Alonso V. Jaques; Francisco Angel; Ma. Belén Barraza

Título (Idioma original) : The Impact of Variable Measurement Spacing in Concentration Profiles Used in Diffusion Experiments

Nombre del Congreso : 10th International Conference on Diffusion in Solids and Liquids – DSL 2014

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TESIS/MEMORIAS

Nº : 1
Título de Tesis : OPTIMIZACIÓN DE MUESTREO ESPACIAL EN EXPERIMENTOS DE DIFUSIÓN EN METALES

Nombre y Apellidos del(de la) Alumno(a) : José Marchant Lillo

Nombre y Apellidos del(de la) Tutor(a) : Alonso Jaques

Título Grado : Pregrado

Institución : Universidad Técnica Federico Santa María
País : CHILE
Ciudad : Valparaíso
Estado de Tesis : En Ejecución
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Nº : 2
Título de Tesis : Implementación de Método de Regularización en Estimación de Difusividad no-Lineal

Nombre y Apellidos del(de la) Alumno(a) : Carlos Cruz Piñeiro

Nombre y Apellidos del(de la) Tutor(a) : Alonso Jaques Solis
Título Grado : Pregrado
Institución : Universidad Técnica Federico Santa María
País : CHILE
Ciudad : Valparaíso
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