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NUMERICAL SIMULATION OF HYDROGEN DESORPTION FROM A MEMBRANE

ABSTRACT - DAPOR M. & MIOTELLO A., 2007 - Numerical simulation of hydrogen desorption from a membrane.

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According to the US Department of energy, global energy consumption will increase by 70% between 2003 and 2030. Among many open challenges: finding new energy sources; satisfying the increasing energetic requirements in full respect for the environment and for population's safety; learning how to use energy with maximum efficiency. One of the open problems, concerning hydrogen storage in metals, is represented by the understanding of the mechanisms related to its desorption from the material. In this work, we present the results of a numerical code realized to simulate the hydrogen desorption processes.

KEY WORDS - Diffusion, Permeation, Desorption, Hydrogen.

RIASSUNTO - DAPOR M. & MIOTELLO A., 2007 - Simulazione numerica del desorbimento di idrogeno da una membrana.

I consumi energetici tra il 2003 ed il 2030, secondo le stime del Dipartimento Statunitense dell'Energia, aumenteranno di circa il 70%. Le sfide aperte sono molte e riguardano la ricerca di nuove fonti energetiche, la necessità di soddisfare le crescenti richieste di energia nel pieno rispetto dell'ambiente e della sicurezza della popolazione, quella di imparare ad utilizzare l'energia con la massima efficienza. Uno dei problemi aperti, che riguarda l'immagazzinamento dell'idrogeno nei metalli, è rappresentato dalla comprensione dei meccanismi relativi al suo desorbimento dal materiale. In questo lavoro presentiamo i risultati di un programma di calcolo realizzato per simulare i processi di desorbimento dell'idrogeno.

PAROLE CHIAVE - Diffusione, Permeazione, Desorbimento, Idrogeno.

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Introduction

The theoretical study of hydrogen desorption from a thin metallic film cannot neglect the occurrence of hydrogen trapping sites [1-4]. Dislocations, microvoids, high-angle grain boundaries, vacancies and matrix-impurities interfaces are all examples of trapping sites. They can be classified as reversible and irreversible traps. If the binding enthalpy of a trap is high enough so that it is very difficult for a captured hydrogen atom to escape from it, the trap is considered as irreversible. Otherwise the trap is treated as reversible. The critical trap depth is the minimum potential depth characterizing the irreversible traps and, at room temperature, it is approximately 0.7 eV per atom. If the potential well is not deeper than 0.7 eV, the trap is a reversible one: it can both capture and release hydrogen atoms. Otherwise a hydrogen atom, once trapped, may no more be released.

The three coupled differential equations governing hydrogen diffusion and trapping have been numerically solved in order to study the desorption processes of hydrogen from thin metallic films.

Theory

Let us consider a one-dimensional metallic sample with uniformly distributed traps. The diffusion of the hydrogen in such a system is governed by a parabolic partial differential equation. Let us indicate with c the hydrogen concentration, with N the number of traps per unit of volume in the membrane and with θ the fractions of occupied traps. Thus

$$\frac{\partial c}{\partial t} + N\frac{\partial \theta}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{1}$$

where D is the diffusion coefficient of the hydrogen in the considered system. In order to describe the evolution with the time of the fraction of occupied traps, let us introduce the quantities k and p which represent the rate of capture and of release per trap, respectively. The evolution with the time of θ can be calculated by

$$\frac{\partial \theta}{\partial t} = kc(1-\theta) - p\theta \tag{2}$$

Let us recall that a trap is considered irreversible when its release rate is infinitesimally small while the capture rate assumes a finite value. In other words an irreversible trap can be considered as a well able to capture atoms of hydrogen without release them. In order to consider both the kinds of traps with their specific parameters, it can be useful to explicitly introduce the time evolution of the occupied fraction of irreversible traps. Let us assume to have N_i irreversible traps per unit of volume in the membrane and indicate by k_i the capture rate per irreversible trap. The previous symbols are now kept to describe the reversible traps. If θ_i is the fraction occupied of the N_i irreversible traps, then

$$\frac{\partial c}{\partial t} + N\frac{\partial \theta}{\partial t} + N_i\frac{\partial \theta_i}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{3}$$

$$\frac{\partial \theta}{\partial t} = kc(1-\theta) - p\theta \tag{4}$$

$$\frac{\partial \theta_i}{\partial t} = k_i c(1-\theta_i) \tag{5}$$

RESULTS AND DISCUSSION

Let us indicate with D the hydrogen diffusion coefficient in the given material and with c_0 the initial concentration in the middle of a membrane whose thickness is a. If J is the permeation flux, let us introduce the non-dimensional permeation flux $j=aJ/Dc_0$. It is a function of the non-dimensional time defined as $\tau = Dt/a^2$, where t is the time. In Figure 1 we have represented the results of our simulation of the non-dimensional flux j as a function of the non-dimensional time τ. Note

that we have represented three cases: the circles, reported for comparative purposes, represent the evolution of the process in the absence of traps (pure diffusion). Squares represent desorption when just the reversible traps are considered, while triangles describe the more general and realistic case in which both the kind of traps (reversible and irreversible) are present.

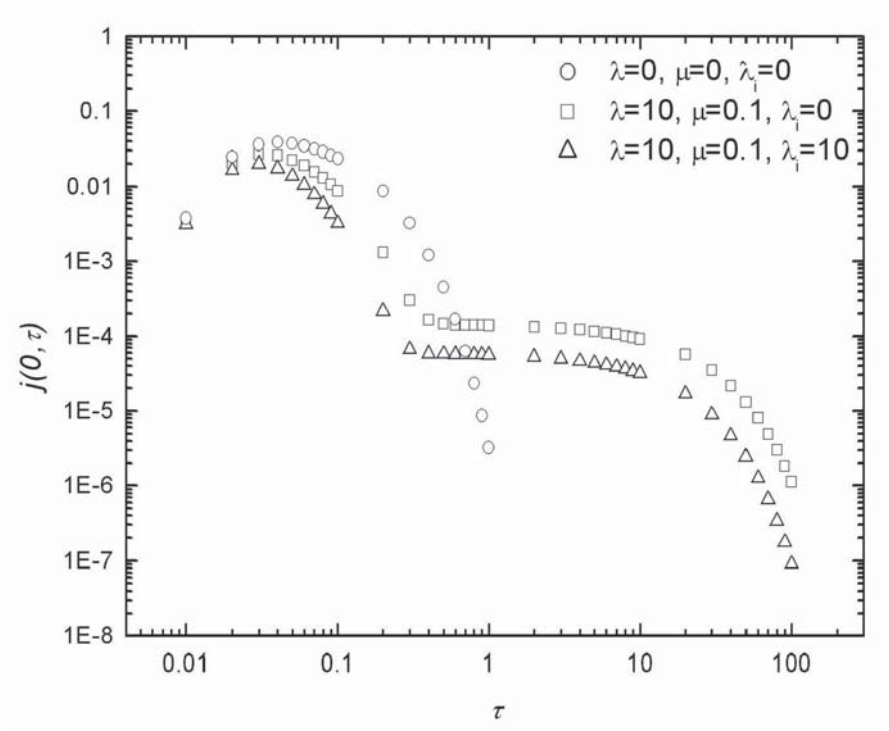

Fig. 1. The non-dimensional permeation flux j as a function of the non-dimensional time τ.

Note that the non-dimensional parameters represented in the figure characterize the trapping sites: in particular λ is proportional to the rate of capture of the reversible traps, λ_i is proportional to the rate of capture of the irreversible traps and μ is proportional to the rate of release of the reversible traps.

Concerning the cases in which the traps are present, i.e. for values of the capture and release rates different from zero, the explanation of the plateau is the following: as the hydrogen atoms move from the middle to the surface of the sample, they may be trapped by the reversible

traps. For this reason the flux, after a decreasing behavior, reaches a steady state value different from zero. It is due to the dynamical equilibrium between the capture of the atoms coming from the middle of the sample and the release of hydrogen by the reversible traps. Once, on the other hand, the number of hydrogen atoms arriving from the middle of the membrane decreases, the reversible traps can capture very few new atoms. Eventually, when the flux of atoms from the middle of the membrane becomes zero, the reversible traps can only release hydrogen atoms until they become completely empty. As a consequence, after an interval of time depending on the values of the parameters characterizing the material, the traps and their distribution in the membrane, the flux begins to decrease until it reaches zero.

It is clear that the implemented numerical code permits the analysis of problems with complicated boundary conditions and/or non-linearity in transport parameters. These extreme conditions, frequently encountered in desorption and permeation experiments, cannot be treated within analytical schemes but can be suitably handled by the present numerical code.

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