Finite Element Method Applied to Mathematical Modelling of the Hydrogen Diffusion Process in Metals

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This paper presents a finite element based method to modeling and simulating the hydrogen diffusion process in metals. Simulation has been done at microscopic level by taking into consideration a regular hexagonal prism as generic geometric model for the metallic grain. In solving the equations system associated to the model, the software package ANSYS10 has been used. Although this software is usually used for conductive heat transfer problems, it has been adapted to solve the hydrogen diffusion problem by identifying analogies between the heat transfer equation and the diffusion equation.

Keywords: Hydrogen diffusion, metallic polycrystal, finite element method, mathematical modeling

The diffusion processes in metals have a significant influence on the metals' properties during the welding process, on the parts joined by welding. Modern concepts [1-3] about physical phenomena in metals during the welding process cannot be applied without having basic knowledge about the diffusion process.

Hydrogen assisted cracking (HAC), frequently referred as cold cracking, represents one of the most important problems that have to be taken into consideration when steels are welded. This problem is especially important for high-strength steels that are used to build rigid structures and/or with thick wall, as it happens in the case of chemical industry equipment.

HAC appears simultaneously or delayed to welding in all the areas of a welded joint. Reference literature [4, 5] is unanimously in considering that HAC appearance is conditioned by the simultaneous occurrence of the following factors:
- presence of diffusible hydrogen, having a concentration above a certain critical value within the area of a mechanical stress concentrator;
- appearance of strong enough mechanical stress;
- existence, in the analyzed area, of fragile microstructures which are likely to crack when hydrogen is present;
- existence of a temperature less than a critical value T_c (mostly, $T_c \leq 100 - 200°C$), which is specific for each case.

Essentially, HAC is a brittle, irreversible, located fracture, which appears at a temperature relatively close to the room temperature or, sometimes well below this. Thus, the name cold cracking is legitimated. Harmful hydrogen, as far as HAC is involved, is the hydrogen dissolved in the metal matrix in the form of positive ions, often in a supersaturated concentration. The hydrogen ion radius is small compared to the parameter of the crystalline network of the dissolvable matrix; therefore an interstitial solution is formed containing the hydrogen ions which are weakly bounded to the metal ions in the crystalline network knots.

Besides its own diffusion, hydrogen transport can be done by the process of dislocations migration. This process can become significant in areas characterized by strong local plastic deformations. Sometimes, in special conditions (e.g. in a hydrogen pore with clean metal surface), a catalytic dissociation (at low temperatures) of the molecular hydrogen into atomic hydrogen, absorption and absorption of the molecular hydrogen and the transport of the hydrogen atoms towards the interior of the metal (by dislocations) could appear [6].

The finite element method (FEM) uses as a starting point an integral model of the studied phenomenon. This model can be directly obtained, by calculations or by using the corresponding derivative model to which one can apply variational calculus or the weighted residuals method [7, 8]. Since an integral model is used with some sets of piecewise continuous functions, FEM will not be anymore conditioned by the existence of a rectangular network. By using the FEM, geometric solids of any shape, with rectilinear and curvilinear frontier, can be discretized.

Due to its high performance, FEM has become an almost standard method used for analysis and design in civil engineering, aerospace engineering and nuclear engineering. Moreover, by having the possibility to finding spatial distributions of parameters in different solids, as well as their time evolution, numerical modeling with finite elements contributes to the developing of a new way of thinking the engineering analysis.

Usually, the finite elements are defined during the discretization process where they appear as a result of analysis domain decomposition into many compatible sub-domains with disjunctive interior. Those sub-domains are connected by knots which are in fact selected points (in the current domain) to which the studied variables or their derivatives are specified.

From a geometric point of view, the finite element ideally reproduces parts of an analyzed real solid. It has a volume and it can be described by some physical properties such as density, viscosity, elasticity, thermal conductivity etc., according to the imposed goal. Functionally, a finite element approximates one or more problem variables in the space occupied by the real part which it models.

Nodal finite elements are the most widely used finite element type and they historically represent the main vain of evolution and development of this numerical method.

They can represent the variation of a field by exclusively using [9-11]:

- a set of nodal values of the approximated function, or of the function and its derivatives to a certain order;

- a set of form functions which are associate to each finite element type.

In other words, the nodal structure of these elements is found during the approximation process of any field of variables.

We present in this paper a simulation study about hydrogen diffusion in metallic polycrystals as an analogy with the case where a thermal field is involved and we are interested to finding the values of hydrogen nodal concentrations and flows.

Experimental part

For simulating the hydrogen diffusion process, by using FEM, the authors of this paper have used the original experimental results [2].

A specimen made on S235JR (SR EN10027-1) steel, electrolytically charged in order to produce a hydrogen trapping, was used. To charge the specimen an experimental platform was designed and built [12-14]. This is composed by: glace recipient; 8 graffito elements, serial connected on c.c. power source with 2.5V voltage and 0.7A current; OL37 piece test connected with graffito elements. To realize electrolytic process on consider OL37 piece test like anode and the cathode is graffito electrodes battery. The piece test is immersing in distillation water solution. This electrolytic filled was realized in approximate 48 h.

After charging, the specimen was microscopically analyzed at granular and inter-granular levels, at different time periods, between 5 and $4320 \, \text{min}$. The method used for evidencing of diffusible hydrogen trapping at microscopic scale, with a drop of cedar oil applied on the specimen surface, was also described in [2]. The evolution in time of the concentrations of diffusible hydrogen (expressed as cm³ hydrogen / 100 g metal) on the grain surfaces and in the inter-granular spaces are presented in figure 1 and figure 2.

The volumetric concentration C_V of hydrogen was calculated according to:

$$C_V = \frac{N \cdot V_{bubble}}{G_{grain}} \cdot 100 \qquad (1)$$

where C_V is the volumetric concentration $[cm^3 / 100g]$, N is the number of hydrogen bubbles, V_{bubble} is the volume of a hydrogen atom $[cm^3]$, G_{grain} is the weight of the considered metal grain (in grams).
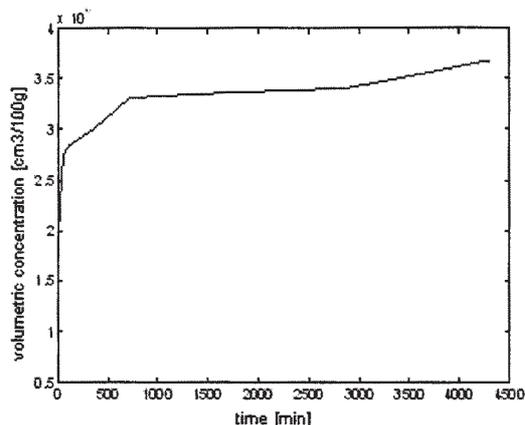

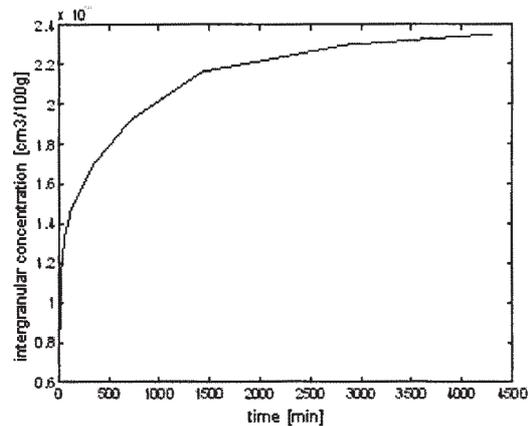Fig. 1 Evolution of volumetric hydrogen concentration in time

Fig. 2 Evolution of intergranular hydrogen concentration in time

The determined volume of a hydrogen bubble was 0.65×10^{-25} cm³, taking into account that the hydrogen bubble radius was 25×10^{-10} cm.

The M_{grain} value is found by taking into consideration the specimen volume, its weight (5.88×10^{-24} g) and the grain volume. The result is:

$$M_{grain} = 14.39 \cdot 10^{-17} \text{g} \quad . \qquad (2)$$

Similarly, values for intergranular concentrations C_g [cm³/100g] have been calculated according to:

$$C_g = \frac{N \cdot V_{bubble}}{G_g} \cdot 100 \, , \qquad (3)$$

where G_g is the intergranular space weight.

The mass transfer process in solids is described by the first Fick's law [10], written in a one-dimensional form:

$$J = D \cdot \frac{dC}{dx} \, , \qquad (4)$$

where D is the diffusion coefficient [cm²/s], J is the atomic flow defined as the number of atoms that go through the area unit in a time unit, dC /dX is the concentration gradient along the X axis.

The atomic flow J can be written also as:

$$J = \frac{n \cdot m_{H_2}}{S \cdot \Delta t} \, , \qquad (5)$$

where n is the difference between the number of bubbles calculated at two consecutive moments, represents the hydrogen atomic mass, S is the grain surface and Δt is the time period.

By using the above equations and numerical data, the values $D_V = 7.5 \times 10^{-17}$ cm²/s and $D_g = 11.1 \times 10^{-12}$ cm²/s have been calculated for the volumetric diffusion coefficient and the diffusion coefficient in the intergranular space, respectively.

The calculated ratio $m_{H_2}/D_V = 1.48 \cdot 10^5$ confirms the correctness of the experimental values found by comparing with the values reported in the literature [14]. These values have been used to obtain a mathematical model based on finite elements of the hydrogen diffusion process in metals, with ANSYS 10 software.

To obtain the mathematical model with finite elements, the aspects described below have been taken into consideration.

The metallic grain has been considered as a polyhedron having all sides regular hexagons with side length of $1.4 \cdot 10^{-6}$ cm. Since such a solid does not mathematically exist (the most complex solid is a regular dodecahedron with regular pentagon as side surfaces), we took into
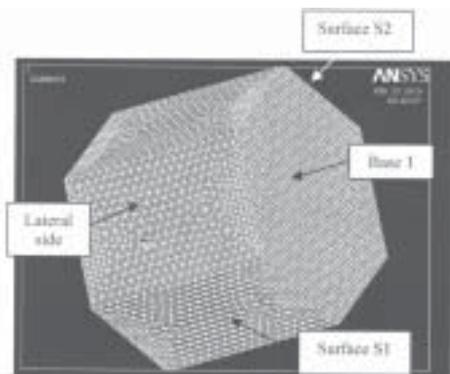
http://www.revistadechimie.ro

Fig. 3 Surfaces of metallic polyhedron taken into consideration for mathematical modelling

$$\lambda_x \frac{\partial T}{\partial x} n_x + \lambda_y \frac{\partial T}{\partial y} n_y + \lambda_z \frac{\partial^2 T}{\partial z^2} n_z + q = 0, \quad \forall N(x,y,z) \in S_q \tag{7}$$

$$\lambda_x \frac{\partial T}{\partial x} n_x + \lambda_y \frac{\partial T}{\partial y} n_y + \lambda_z \frac{\partial^2 T}{\partial z^2} n_z + \alpha(T - T_\alpha) = 0, \quad \forall P(x,y,z) \in S_\alpha$$

In the equations above, V is the volume of the analyzed field and S is the external surface of this domain. If S_T, S_q and S_α are the boundary segments on which the temperature T, q is the unitary thermal flow and   is the convection coefficient, one can write:

$$S_T \cap S_q = \varnothing; \quad S_T \cap S_\alpha = \varnothing; \quad S_q \cap S_\alpha = \varnothing \tag{8}$$

In equations (11), (12), (13), the following notations have been used: $T(x,y,z,t)$ is the temperature function, λ_x, λ_y, λ_z are the thermal conductivity components on x, y, z directions respectively, ρ is the material density,   is the material specific heat, T_0 is the initial temperature distribution in the analyzed domain V, $g(x,y,z)$ represents the temperature spatial distribution on the boundary segment S_T, q is the thermal flow on the boundary segment   , α is the heat transfer coefficient between the fluid and solid materials on the boundary segment   , T_α is the washing surface fluid temperature S_α, Q_0, represents the heat source term, n_x, n_y, n_z are the component of the unity vector normal to the heat exchange surface on directions respectively.

We use the following equation for the hydrogen diffusion in metal polycrystals:

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right) + \frac{\partial H_V}{\partial t} \tag{9}$$

with the initial and limit conditions below:

$$C = C_0 = 0, \quad t \le 0 \tag{10}$$

$$C = C_S(x,y,z), \tag{11}$$

consideration a regular hexagonal prism, having the base side length $a = 1.4 \cdot 10^{-6}$ cm and the height $h = 2.2 \cdot 10^{-6}$ cm, as geometrical model for the metalic grain (fig. 3).

The following physical properties have been considered: specific heat capacity $c_p = 0.63 \times 10^{-5}$ J/(g.K), steel density, 7.9×10^6 g/m^3 volumetric diffusion coefficient $D_v = 7.5 \times 10^{-17}$ cm^2/s and intergranular diffusion cofficient $D_g = 11.1 \times 10^{-12}$ cm^2/s.

Model discretization has been done by dividing each side length into 20 intervals, by using 10 peaks tetrahedra. Finally, the model contained 217,113 knots.

For the mathematical model, the 3rd type boundary conditions have been used, with known input and output concentration flows. Those flows were identified for each moment (5 min, 15 min, …, 4320 min) and they correspond to the moments of experimental observations previously described. Also, hydrogen concentrations on a side surface of the prism (C_2) and on a prism base surface (C_1) were used as initial conditions.

ANSYS 10 software has been used to solve the elementary equations system. This software is often used for solving conductive heat transfer and, for the purpose of this paper, it has been adapted for solving the problem of hydrogen diffusion by identifying the analogies between the heat transfer equation and the diffusion equation.

The heat transfer equation is:

$$-\rho c_p \frac{\partial T}{\partial t} = \lambda_x \frac{\partial^2 T}{\partial x^2} + \lambda_y \frac{\partial^2 T}{\partial y^2} + \lambda_z \frac{\partial^2 T}{\partial z^2} + Q_0, \tag{6}$$

with the initial and limit conditions below:

$$T = T_0, t \le 0$$
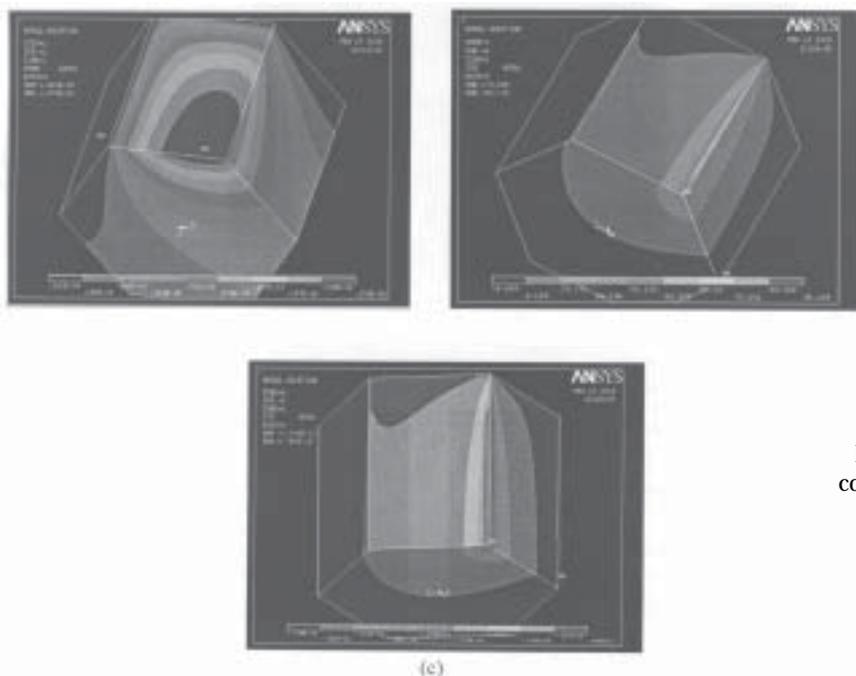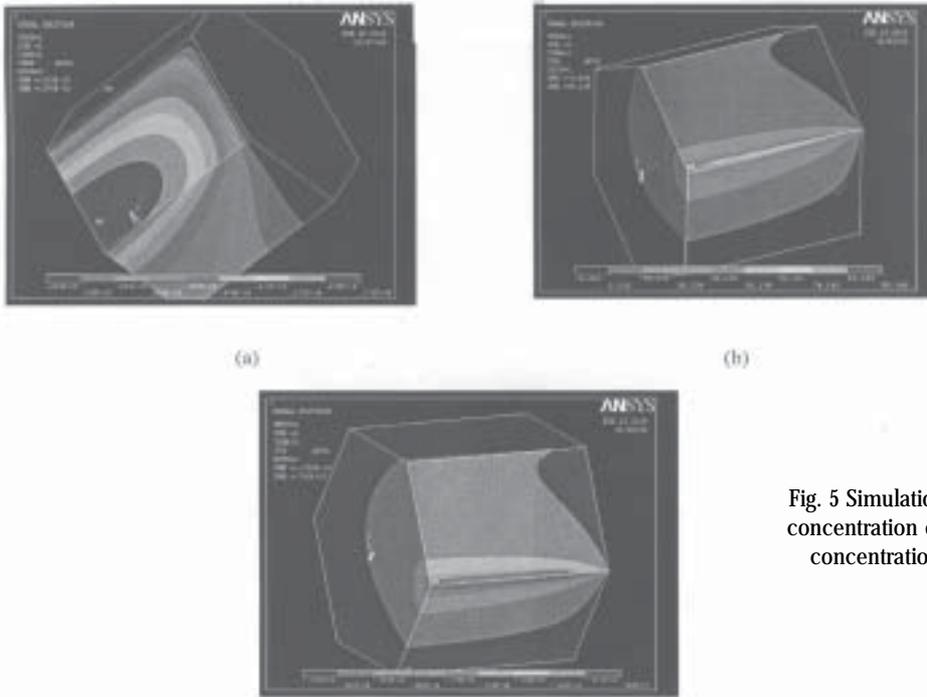$$T = g(x,y,z), \quad \forall M(x,y,z) \in S_T$$

(c)

Fig. 4 Simulation results at 5 min. (a) Hydrogen concentration distribution along the X axis, (b) the concentration gradient, (c) the hydrogen flow.

(a)   (b)

Fig. 5 Simulation results at 2880 min. (a) Hydrogen concentration distribution along the X axis, (b) the concentration gradient, (c) the hydrogen flow.

(12)

In the above equations we denoted C as the local hydrogen concentration (cm³ hydrogen / 100 g metal), x, y, z represent the spatial coordinates of the point taken into consideration, [cm³ hydrogen / 100 g metal] is density of the hydrogen wells or sources.

The following similarities of heat transfer and mass transfer by diffusion have been found:

$$D_v \frac{\partial C}{\partial x} n_x + D_v \frac{\partial C}{\partial y} n_y + D_g C n_z + J = 0.$$

- the volumetric diffusion coefficient D_v corresponds to the ratio between thermal conductivity and the product of density and specific heat capacity, $\lambda / (\rho \cdot c_p)$;

- the diffusion coefficient D_g is similar to the convection coefficient, α.

It is worth mentioning that the diffusion process was supposed to act in an homogeneous and isotropic environment, therefore the physical and mechanical properties remain unchanged.

Results and discussions

Simulations have been done for multiple time values but, in this paper, only moments t = 5 min and t = 2880 minhave been chosen to describe the results..

At the moment t = 5 min the hydrogen concentration distribution, the concentration gradient distribution and the hydrogen flow, in the analyzed grain, on OX direction, have the shape presented in figure 4.

These results have been obtained for the following initial and limit conditions:

$$C_1 = 0.1 \cdot 10^{-9} \, cm^3 / 100g$$

$$C_2 = 0.65 \cdot 10^{-10} \, cm^3 / 100g$$

$$J_1 = 0.76 \cdot 10^{-15} \, mL / 100g \cdot cm^2 \cdot s$$

$$J_2 = -0.002 \cdot 10^{-15} \, mL / 100g \cdot cm^2 \cdot s,$$

where C_1 is the concentration on the prism base 1, C_2 represents the concentration on a lateral surface, J_1 is the input flow on surface 1 and J_2 is the output flow on surface

2. These notations have been used during the modeling process.

One can observe an area which is strongly influenced by the concentration flow entering surface S1; then, the most depleted area in terms of concentration is the area between the grain middle part and the space which is opposite to the input flow. The hydrogen infusions from the intergranular region towards the inner part of the grain are done on a direction which is perpendicular to the direction of the intergranular space.

Simulation results at t=2880 min are shown in figure 5.

To calculate the average concentration value, this sequence of values was translated in the Microsoft Excel 2007 where it was generated this value for each time point considered. By analyzing the temporal variation of the ratio of the two concentrations, there is an evolution of it, followed by an involution (fig.6).
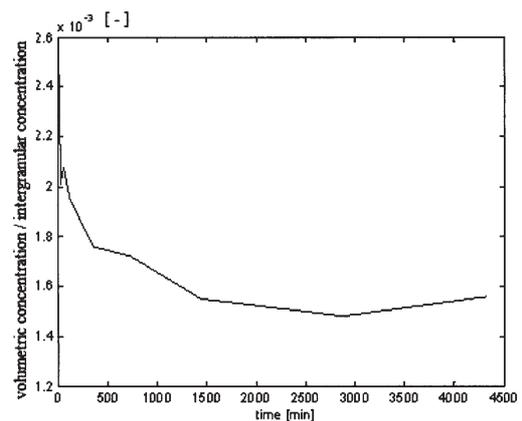

Fig.6 Time evolution ratio of hydrogen concentrations

We can make the following observations regarding the distribution of hydrogen concentrations in grain volume and intergranular space:

-in the first 15 min it appears that a large amount of hydrogen is present inside the grain;

- after this time, we suppose that some of this hydrogen amount migrates from the inside of the grain to intergranular spaces, which leads to descent of the variation curve.
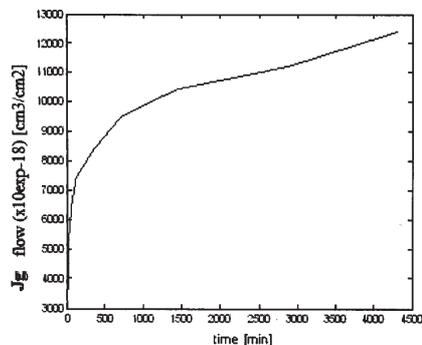
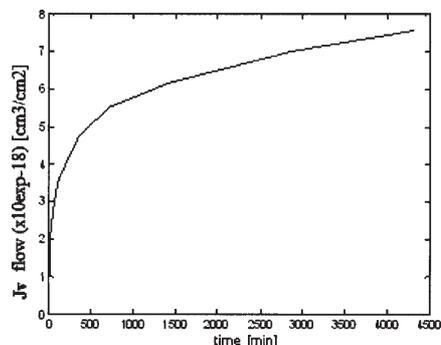Fig.7 The variation in time of flow on the intergranular spaces

Fig.8 The variation in time of flow on the surface of grains

- after about 2800 min , there is a return to the trend of increasing the concentration of hydrogen inside the grain in relation to intergranular concentration.

From the analysis of concentration gradients diagram we see that minimum values of concentration gradient appear on the X-axis direction, while for the other two directions we distinguish essential increase of concentration gradients. Mention that the Ox direction is the direction of propagation of the flow concentration.

According to performed experimental data regarding the values of volumic and intergranular concentrations measured at different times, it was found that the ratio of intergranular diffusion coefficient and volumic diffusion coefficient has a very high value:

$$\frac{D_g}{D_V} \geq 10^5 \qquad (13)$$

This high value is valid in classical theory for crystals with a radius of less than 10^{-3} mm.

Thus, it can be said that the diffusion currents exist much stronger on the grain boundaries than inside it. Even if the concentrations at the boundary between the grains are much higher than the levels from inside the grain, it is found that a significant amount of hydrogen was transported with these strong intergranular diffusion currents inside the grain. A reverse phenomenon is found in the case of the flow concentration. The dependences on time of the flow on the intergranular spaces and on the grain surface are shown in figure 7 and figure 8, respectively.

From these observations we can conclude that the preferential areas for hydrogen atoms migration are represented by the intergranular spaces of grains. Inside the grains there are smaller quantitative displacements of the hydrogen atoms than the grain geometric dimensions.

It is noted that the number of hydrogen bubbles distributed in the body of grains represents 60-75% of the total number of the hydrogen bubbles produced by the diffusion process while the remaining proportion represents the hydrogen bubbles distributed in the areas of intergranular spaces.

From 3D analysis was observed that the areas of maximum concentration of diffusible hydrogen are areas in the vicinity of the triple point (the intersection of intergranulaer spaces with grain surfaces), which is the maximum concentrator area of diffusible hydrogen on a microscopic scale.

According to data from 3D representations, in the triple point areas these maximum concentrations have values between 940 and 1800 cm^3 hydrogen / 100 g metal.

Conclusions

It can be concluded that in metallic polycrystals the diffusion process of hydrogen within the microscopic scale is manifested both on grain (metallic crystal) and on grain boundaries. An important role has hydrogen stream on intergranular spaces, namely the flow of hydrogen atoms on the intergranular spaces represents 96% of the total flow of hydrogen.

Thus, the diffusion coefficient of hydrogen through the polycrystals is a weighted average of the diffusion coefficients on grains body and on intergranular spaces, relative to their surface.

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