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Palladium coating on quenched-tempered martensitic steel for hydrogen electrochemical permeation tests

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Abstract

A coating process is proposed to obtain a thin palladium layer on high-strength steel. The quality of the layer is investigated by SEM observation.Potentiokinetic curves are performed to ensure no hydrogen formation during the coating process. Coated samples are tested by hydrogen permeation test and compared to non-coated samples. Permeation data analysis and boundary conditions are discussed based on permeation results and 1D simulations.

*Keywords:*Palladium coating, High strength steel, Hydrogen permeation

I. Introduction

Hydrogen mobility and trapping in metals can be study by electrochemical permeation (EP) of hydrogen. This method was firstly developed by Devanathan and Stachurski in 1962[1] and it has been widely used on several metals[2–15].It is very accurate [16] as long as boundary conditions are perfectly known. Indeed, hydrogen entry and detection are modified by surface processes. For steels, the oxide layer on the detection side acts as a barrier and limits the stabilised hydrogen flux[2, 3, 17]. But the stability of this oxide layer is a proof that hydrogen oxidation takes place at the oxide/metal interface [17, 18]. So there is a modification of the diffusion of hydrogen in the metal by the hydrogen ion in the oxide layer[19]. In addition to this, complete oxidation of the hydrogen flux at the detection side is not fulfilled on iron or steel surfaces [4].

Moreover, during the desorption transient, due to the oxide barrier at the detection side, hydrogen desorption by the charging side increases, and detected hydrogen decreases. On the charging side, the oxide layer spontaneously formed before EP test is reduced during hydrogen charging[17]. As hydrogen absorption rate is strongly related to the coverage of hydrogen adsorbed on the surface, any modifications of this surface change hydrogen flux.

A solution to ensure boundary conditions during EP test is to use a palladium coating [20]. This metal is totally stable in solutions of permeation cells (NaOH 0.1M) and the diffusion coefficient of hydrogen is close the one of steels [16].Many coating methods exist, but sometimes require a heating step during the process. As the microstructure of the steel is metastable, this kind of heat treatment is prohibited, to keep the original microstructure, i.e. the same hydrogen traps sites distribution.

An electrochemical process to obtain a thin palladium coating on high-strength steel is presented. The best coating conditions are determined thanks to Hull cell tests and potentiokinetic curves. The quality of the coating is investigated by scanning electron microscopy (SEM) observations. Finally, EP tests are performed to compare the results with or without the coating on the detection side. A diffusion model is used to determine the hydrogen concentration profile in both cases.

II. Material and experimental procedure

II.1 Material

The material of the study is a high strength steel S690QL (EN 10137-2). It exhibits a tempered martensitic microstructure consisting of laths of about 200 nm width. Laths are gathered in blocks and packets which are contained in prior austenite grain with a cluster size ranging from 10 to 20 μm. The steel chemical composition is given in table 1. The tempering consisted in two hours at 550°C after austenitization at 920°C and water quenching. No retained austenite was revealed by X-ray analysis.

Table 1: Chemical composition of steel S690QL (wt. %)

Elements	C	Si	Mn	Mo	Nb	Ni	Ti	S
wt.%	0,16	0,33	1,22	0,25	≤0,10	0,11	≤0,05	≤0,001
Elements	P	V	Zr	N	B	Cr	Cu	Fe
wt.%	≤0,02	≤0,1	≤0,1	≤0,015	≤0,005	0,29	≤0,1	Bal.

This low-alloyed steel is susceptible to general corrosion in aqueous or acid environment. It exhibits a passivity state in alkaline media.

II.2 Coating process

An electroplating bath for plating a coating of palladium is prepared with $PdCl_2$ salt ($5g.L^{-1}$), ammonia (4.2M) and water. Some millilitres of commercial surface active agent are added to improve the wettability of the solution on the steel surface and quality of the coating. Final solution pH is 12.1. This high pH is needed to displace the water reduction reaction (hydrogen formation) to more negative potentials, necessary condition to ensure no hydrogen formation during the process.

For the coating process, a Platinumelectrode and saturated calomel electrode (SCE) are used as the counter and the reference electrodes.The working electrode is a cylindrical sample of 8mm of diameter encased in polyester. The contact surface is about 0.5 cm².

Surface preparation consists in mechanical polishing with SiC paper up to 4000 grade, degrease in ethanol and in some cases anodic pickling in H_2SO_4(30%) solution.

II.3 Hull cell tests

Electrochemical conditions for the coating process can be investigated with Hull cell tests. The cell, presented on figure 1, has a specific geometry to obtain a variation of the current density along the sample. It depends on the applied current and is given by an abacus.

Fig.1. Normalized Hull cell

An applied current of 200 mA is chosen to obtain a current density from 2 to 8 mA/cm². The time of deposition varies from 1 to 3 minutes. X-Ray Fluorescence (XRF) is used to evaluate the palladium thickness along the sample considering homogeneous palladium coating on iron-based substrate. SEM observations are performed to analyze the quality of the coating.

II.4 Potentiokinetic curves

In addition to tests in Hull cell, potentiokinetic curves are made to determine the potential of hydrogen formation. Indeed, absorption of hydrogen during the coating process could modify the permeation curve and lead to a misinterpretation of the results.

Potentiokinetic curves are performed in the electroplating bath with the same sample geometry and electrodes as for the coating process. A scan rate of $5 mV.s^{-1}$ is chosen, starting from the free potential to more negative potentials.

II.5 Electrochemical permeation test

EP tests are performed in a two-compartmental set-up consisting of a charging cell and an oxidation (or detection) cell.Both cells are filled with 0.1M sodium chloride solution deoxygenated by nitrogen. The steel sample is a thin cylindrical membrane with a thicknessl_s of about 0.6 mm and a diameter of 40 mm. The same surface preparation as for coating process is performed (mechanical polishing up to 4000 grade SiC paper).The membrane is mounted in a holder which reduces thecontact surface to a circular area of 1cm² on both faces. This holder can be independently attached to each cell. Platinum counter electrode and saturated calomel electrode are used in both cells and the steel sample is the common working electrode. A floating ground galvanostat is plugged to the charging cell and a potentiostat to the detection side.

The detection side is continuously polarized at -400mV/SCE for non-coated samples and -100mV/SCE for palladium coated surfaces. The potential is lower without the coating to limit the oxide growth at the detection side. In the first case, stabilization of the current at about 0.1µA.cm^{-2} is attended after almost 12 hours. When the steady-state is established, instantaneously with palladium coating, the charging cell is connected to the holder and the charging side of the sample is subjected to a cathodic current (-5 to -60 mA/cm²). The recorded anodic current on the detection side is the permeation rate of hydrogen through the membrane.

II.6 Modelling

The mathematical modelling of hydrogen diffusion through a layer composed of steel with thickness l_s = 0.6 mm and a thin layer based on the 1st and 2nd Fick's laws is analysed. Two kinds of layer are investigated. The first one is palladium coating with thickness of 230 nm and a diffusion coefficient 7.10^{-11}m².s^{-1}[5], the second one is an oxide layer of 2.6 nm thick with a diffusion coefficient of $1.4.10^{-22}$ m².s^{-1}[19].

Hydrogen diffusion in steel as proposed by Sofronis[21] is expressed by a nonlinear diffusion equation (Eq.1)presented below, where Ω_L is the lattice (steel) domain.

$$\forall x \in \Omega_L: \quad \left(1+\frac{C_T(x,t)}{C_L(x,t)}\left(1-\frac{C_T(x,t)}{N_T}\right)\right)\frac{\partial C_L}{\partial t}(x,t) = \nabla.\left(D_L \nabla C_L(x,t)\right) \qquad \text{Eq.1}$$

C_T and C_L are respectively the trapped and lattice hydrogen concentration. N_T is the number of trapping sites. The apparent lattice diffusion coefficient $D_{eff}$is calculated from Eq.2:

$$D_{eff}\left(C_L(x,t), C_T(x,t)\right) = \frac{D_L}{1+\frac{C_T(x,t)}{C_L(x,t)}\left(1-\frac{C_T(x,t)}{N_T}\right)} \qquad \text{Eq.2}$$

D_L is the true lattice diffusion coefficient without effects of trapping.The diffusion coefficient is constant in the coating and no trapping occurs.

The boundary condition at entry side is constant hydrogen concentration C_0=15 mol.m^{-3}(1.9 wppm) and C=0 at exit side. The trapping is simulated with a trap density N_T= 50 mol.m^{-3} and a trapping energy ΔE_T= 20 kJ.mol^{-1}. Fully implicit 1D conservative finite volume numerical simulation is performed over 2000 seconds (50 increments) with our numerical software written from the ground in C++.At each time-step the algebraic nonlinear system that takes into account the coupling between hydrogen concentration in the lattice and coating layer is iteratively solved by a fixed point method which converges in less than 5 iterations. Influence of the mesh size and time-step over the computed solution is investigated in order to ensure that the retained numerical solution is grid independent. 1000 elements are finally used for the steel domain and 100 for the layer.

III. Palladium coating

III.1 Electrochemical conditions for coating

Two examples of SEM observations of sample tested in Hull cell are presented on figures 2a and 2b.

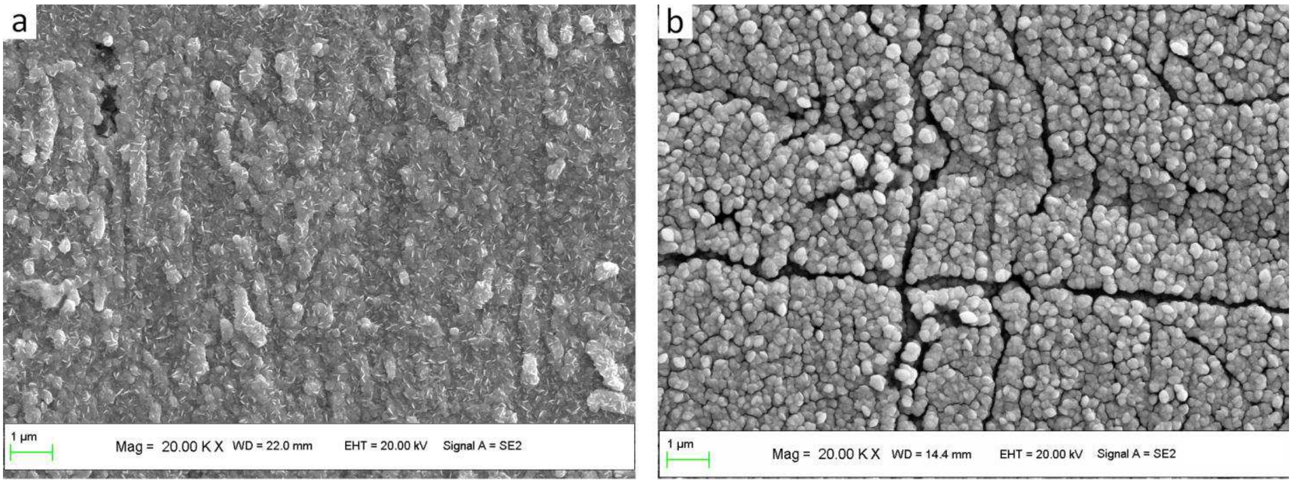

Fig.2. SEM observations of steel surface plated with palladium coating at (a) 2 mA.cm^{-2} during 2 minutes (thickness ≈ 0.2 µm) and (b) 8 mA.cm^{-2} during 2 minutes (thickness ≈ 0.3 µm)

For a current density of 2mA.cm^{-2}, 3 minutes are required to cover the entire surface. On the contrary, at 8mA.cm^{-2} the surface is entirely coated after 1 minute. But cracks appear as the thickness of the coating grows and the current density increases.

A potentiokinematic curve, presented on figure 3, shows the formation of hydrogen by water reduction at a potential of about -950mV/SCE. It corresponds to a current density of 5mA.cm^{-2}.

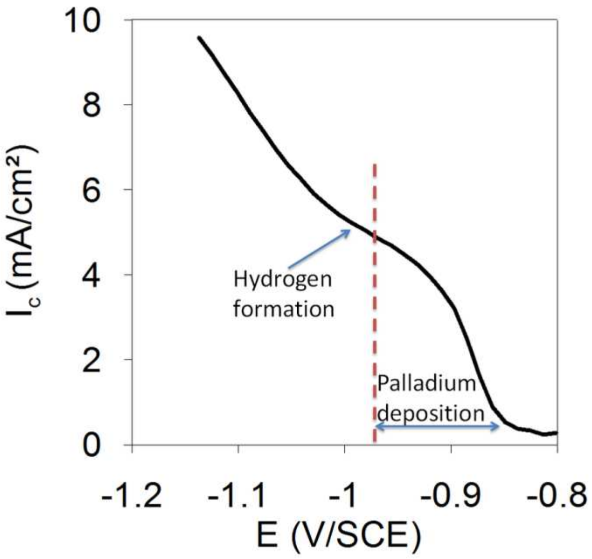

Fig.3. Potentiokinetic curve in palladium electroplating bath at a scan rate of 5 mV/s

To conclude, the best electrochemical conditions to coat a thin palladium layer are from 2 to 4mA.cm^{-2} during 1 to 4 minutes.

III.2 Analysis of the coating

Steel samples were coated with palladium at a current density 4mA.cm^{-2} during 2 minutes. Both cross-section and surface observationswere performed by SEM (see fig. 4).

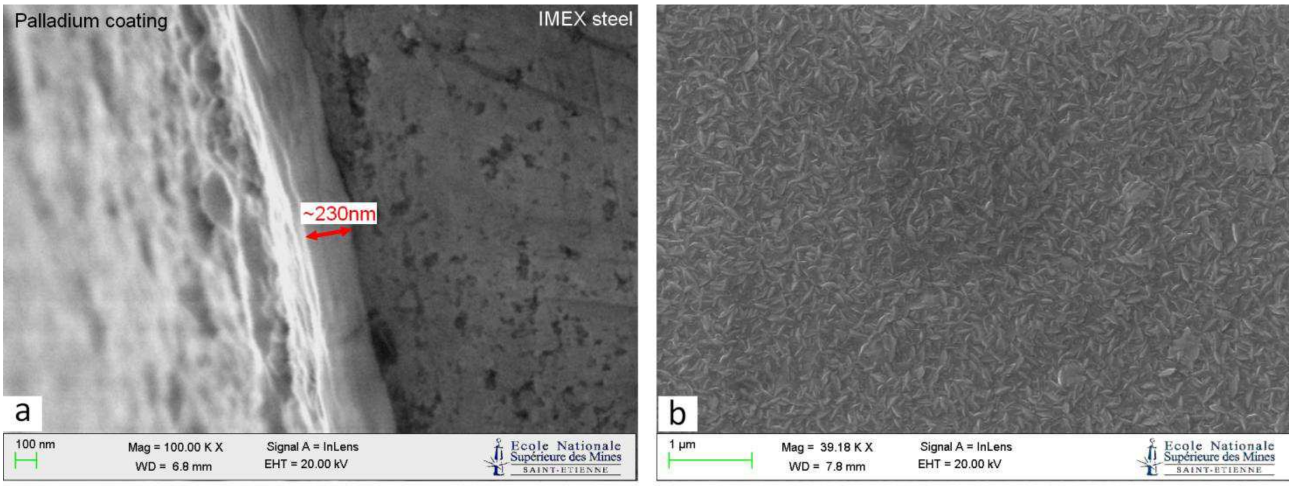

Fig.4. (a) cross-section observation and (b) surface observation of the palladium coating by SEM

The thickness was determined by XRF and image analysis. The average value determined from both techniques is identical and equal to 230nm in these coating conditions.Adherence is tested with an adhesive tape. It could be improve for thicker coating with a heat treatment, but it has been excluded for this steel. The coating is homogeneous, dense and adhesive, so perfectly adapted for hydrogen permeation applications.

IV. Electrochemicalpermeation tests

Permeation tests were performed on coated and non-coated specimens. The first rise transients and last decay transientsare compared on figures5 and 6 respectively.

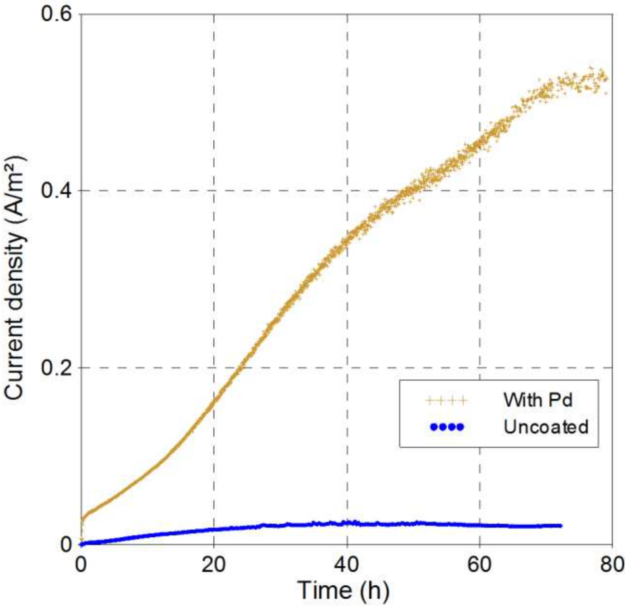

Fig.5. First rise transient of permeation test for uncoated and palladium coated samples

The current density at steady-state is quite more important with the palladium coating (0.53A.m^{-2}) than for uncoated sample (0.024A.m^{-2}). In the one hand, the oxide layer seems to act as a barrier [19]. In the other hand, the hydrogen flux oxidation seems to be more complete with palladium for two main reasons: the hydrogen oxidation reaction is easily on palladium than on iron surface [4], and an higher oxidation potential is applied on palladium coating due to its higher stability than the raw steel.

The rise transient (fig.5) differs from the Fick model in both cases. Indeed, stable charging conditions are not fulfilled at the beginning of the test. Native oxide on charging side is progressively reduced by cathodic current and there is a direct relation between the permeation current and this oxidation state [17]. Palladium coating on the charging side was tested with the same deposition process to remove this phenomenon. But the coating is deteriorated quite rapidly by hydrogen bubbling. A thicker coating is necessary by probably another coating process.

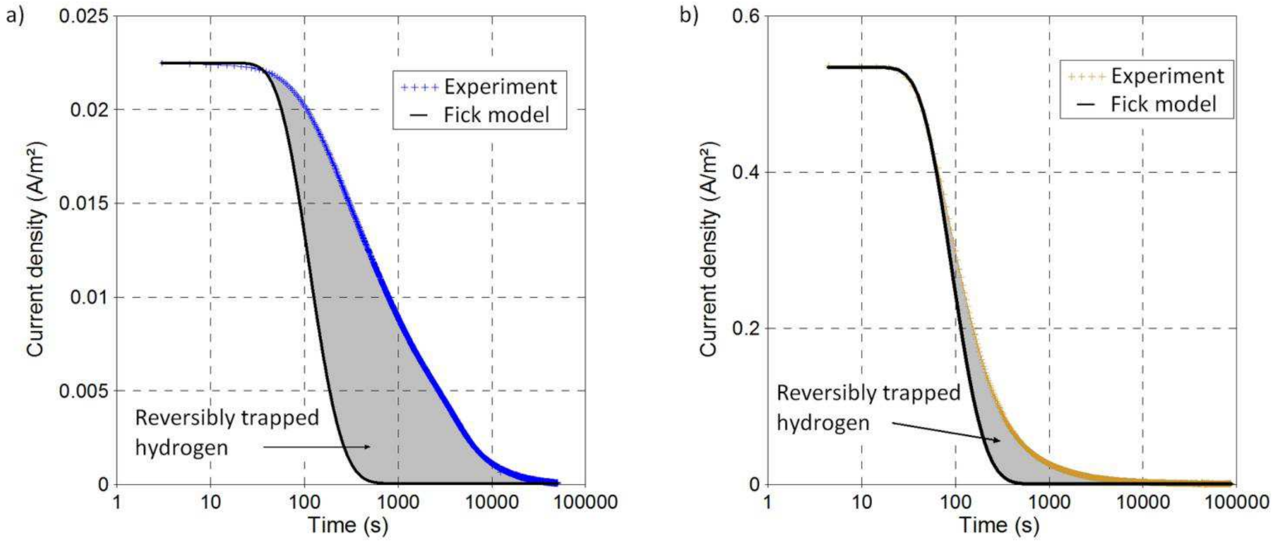

Fig.6. Last decay transients for a) uncoated and b) palladium coated specimens

The concentration of reversibly trapped hydrogenis determined as proposed by Zakroczymski[7](see fig. 6). The apparent lattice diffusion coefficient, used for the Fick model, is determined by partial decays and build-ups (see fig. 7).The applied current density varies from 2 to 60 mA.cm^{-2}. Results are similar for all investigated transients.

The apparent lattice diffusion coefficient is quite similar with or without the palladium coating$\overline{D_L} \approx 5 \times 10^{-10} m^2.s^{-1}$ and is consistent with literature for various ferriticsteels[7, 8, 10, 13]. As a result, the concentration of hydrogen reversibly trapped in the uncoated and palladium coated specimens are 0.115wppm and 0.34 wppmrespectively, with the assumption that no desorption occurs on the charging side. This condition is probably not fulfilled here, and desorption on both faces should be more consistent. But to evaluate the ratio of desorbed hydrogen through each side, the hydrogen concentration profile before desorption have to be known.

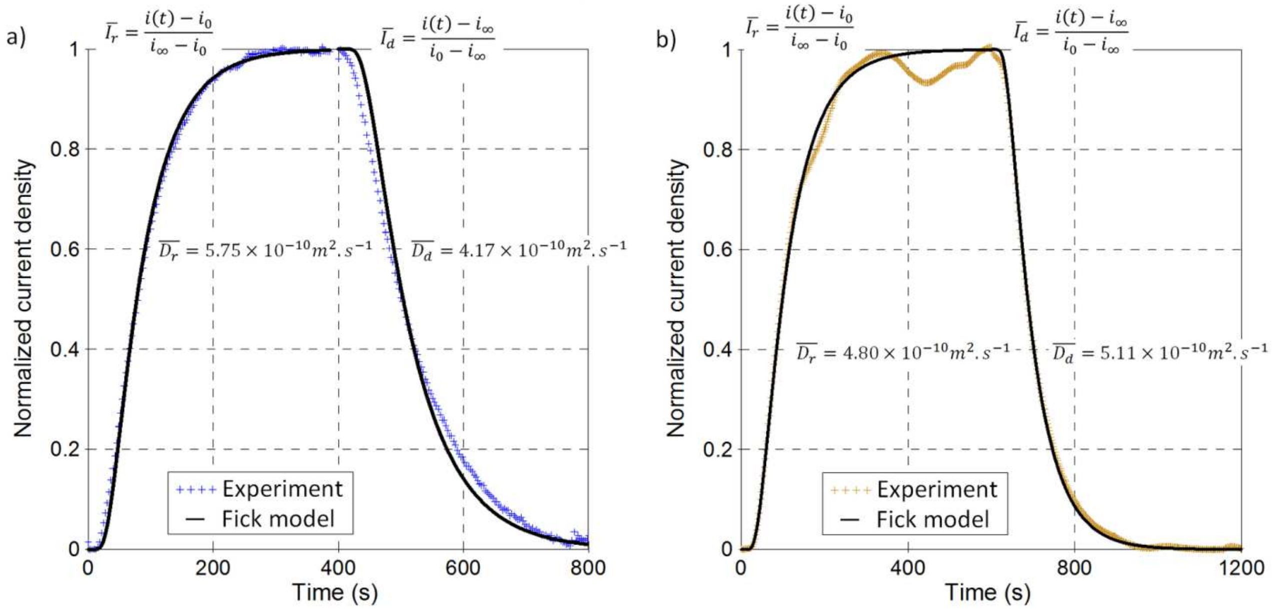

Fig.7. Representative permeation partial transients for a) uncoated and b) palladium plated specimens

This profile is evaluated in both cases by 1D finite elements simulation. Results are presented in figure 8. As expected, with an oxide layer, the concentration is quite homogeneous at steady-state, whereas the profile is linear with the palladium coating. The lattice concentration for the uncoated specimen is equal to the concentration at the entry side, while it is the half for the palladium coated one. The concentration atentry side subsurface can be evaluated with permeation test thanks to the equation[7]:$C_{H,0} = i_\infty . l_s / F . D_L$ with i_∞ the steady-state permeation current density, l_s the thickness of the steel membrane, F the Faraday constant and D_L the apparent lattice diffusion coefficient. As a result, the lattice hydrogen concentration in the uncoated and palladium plated specimens are respectively about 0.04wppm and 0.41wppm.

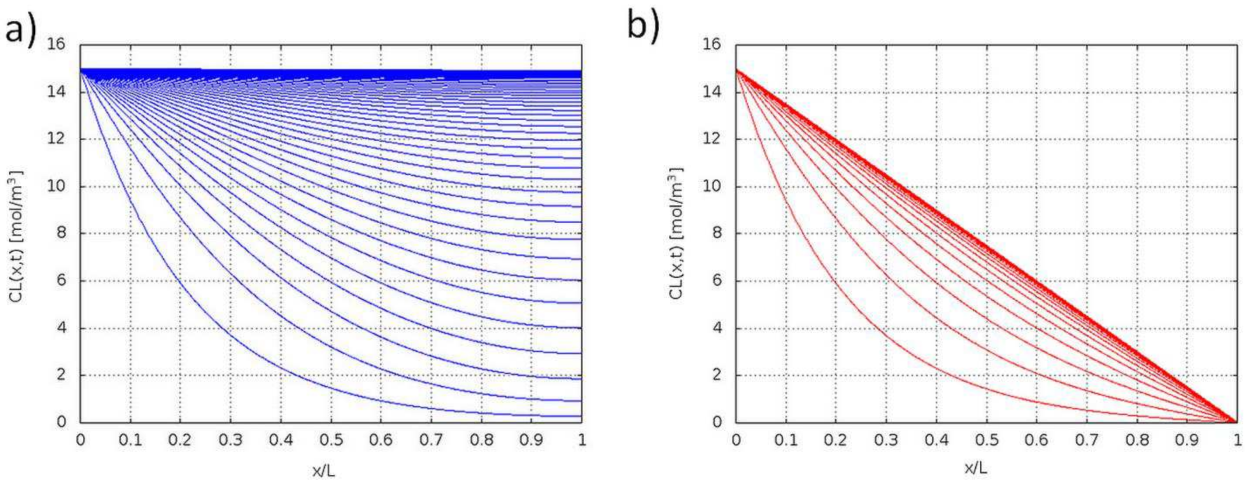

Fig.8. Simulations of the hydrogen concentration in steel membrane during charging in a) uncoated and b) palladium plated specimens

If hydrogen is considered to desorb similarly from entry and exit side during desorption, only 1/3 of the hydrogen amount will escape from the exit side with the palladium coating, while 1/2 will desorb for the uncoated specimen. So, the concentration of hydrogen reversibly trapped in the uncoated and palladium coated specimens are respectively 0.23 wppm and 1.02 wppm. Ratios of hydrogen reversibly trapped over lattice hydrogen are 5.2 and 2.5 respectively for uncoated and palladium plated specimens. Over estimation of reversibly trapped hydrogen is attended with an oxide layer.

V. Conclusions

Conditions for an electrochemical palladium coating process are determined to plate a low carbon steel with a thin layer of palladium. The quality of the coating is investigated by SEM observations. Optimal conditions are determined to obtainhomogeneous, dense and adhesive layer, without producing any hydrogen during the process. Electrochemical permeation tests are compared with uncoated and palladium plated specimens. The ratio of reversibly trapped hydrogen over lattice hydrogen is evaluated, using simulation. This ratio looks overestimated without palladium coating.

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