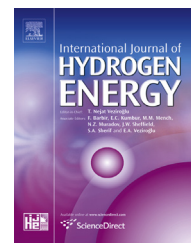


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# Hydrogenation method based on electrodeposited layers controlling the hydrogen desorption rate

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## ABSTRACT

An innovative hydrogenation method to investigate the hydrogen embrittlement of metals and alloys is hereby presented. The benefits of electroplating samples with copper and nickel prior to gaseous hydrogenation at mid-range temperatures are quantified. It is shown that these electrodeposited layers allow to control the hydrogen desorption rate occurring after hydrogenation, during the cooling of the hydrogenated specimen. The present study demonstrates the capability of the method to control the introduced total hydrogen concentration within a margin of 0.2 wt.ppm. The applicability of the described method to further investigations into hydrogen concentrations effects on hydrogen embrittlement of ferritic alloys by the means of mechanical tests is evaluated.

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## Introduction

The hydrogen effects in numerous metals and alloys have been intensively investigated through the past decades, especially to answer industrial concerns [1–6]. In particular, it is now well established that hydrogen embrittles ferrous alloys. Macroscopic effects of hydrogen on the ductility and on the rheology are both reported. The macroscopic hydrogen effects are very sensitive to experimental conditions, especially to the hydrogen charging conditions. For instance, both hardening [7,8] and softening [9–11] are reported in case of cathodically hydrogen charged pure  $\alpha$ -iron, whereas no effects on the rheology are observed in cases of any ferritic steels after gaseous hydrogenation [12,13]. Several studies put in evidence the strong influence of the hydrogen

concentration on the macroscopic behavior of  $\alpha$ -iron [10,14]. Moriya et al. [10] first stated the existence of a critical hydrogen concentration, without being able to estimate it, below which a hardening of pure  $\alpha$ -iron is observed, and above which a softening is obtained. This demonstrates the interest of characterizing the hydrogen effects on the mechanical properties of the materials as a function of known and controlled hydrogen concentrations. Hydrogen charging by cathodic polarization does not allow adjusting precisely the introduced hydrogen concentration. Moreover, strong hydrogen concentration gradients in the hydrogenated sample have been reported [15,16] and microstructural defects can be introduced in the material, depending on the electrochemical conditions [17]. Gaseous hydrogenation allows modifying accurately the introduced hydrogen concentration by tuning the temperature and the hydrogen pressure in the

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**Table 1 – Chemical composition of the ferritic steel X14CrMo17 (in wt.%).**

C	S	Si	Mn	P	Cr	Mo	Ni
0.11	0.35	0.17	1.38	0.025	16.57	0.26	0.38

autoclave. However, gaseous hydrogenation generally leads to the introduction of smaller amounts of hydrogen in the samples than cathodic polarization.

In case of mechanical tests carried out after hydrogen charging, special care must be taken to avoid the desorption of hydrogen out of the samples. This is especially true in case of hydrogenated ferritic materials, due to the low solubility (4.02 wt.ppm at 723 K and 200 bars [18]) and the high diffusivity ( $9.6 \times 10^{-5} \text{ cm}^2/\text{s}$  at 298 K [18]) of the hydrogen atoms in  $\alpha$ -iron. Therefore, a specific experimental method has to be applied to control the outgassing, and consequently the hydrogen concentration, in case of ferritic specimen undergoing tensile tests after gaseous hydrogenation. This is the object of this study.

## Experimental

### Material

The material used for this study is the ferritic steel X14CrMo17 supplied in rod end bars of 20 mm diameter. The bars are annealed at 723 K during 48 h. Tensile test samples of diameter 5 mm and cylindrical hydrogen titration samples of 20 mm diameter and 20 mm height are machined. The chemical composition of the steel is given in Table 1. A large amount of MnS precipitates is present and the mean grain size is about 20  $\mu\text{m}$ .

### Electroplating and hydrogenation

The use of thin deposited layers of different materials on the surface of tensile specimen to reduce the hydrogen desorption after electrolytic hydrogen charging, or the hydrogen adsorption during in situ gaseous hydrogenation tests, has already been developed [19–21]. In the hereby described method, nickel and copper electrodeposited layers are realized on the tensile test specimen and on titration samples before gaseous hydrogenation. The hydrogen solubilities and diffusivities in nickel, copper and  $\alpha$ -iron are presented in Table 2 for comparison. The samples are firstly mechanically polished with a diamond paste 1  $\mu\text{m}$ . Then, the samples are either coated with a Ni or Cu layer, or non-coated. Before electroplating, each sample is etched in 30%  $\text{H}_2\text{SO}_4$  solution and the sample's mass loss is kept between 0.3% and 0.5%. The

**Table 2 – Diffusion coefficients  $D$ , and solubilities  $S$  of hydrogen in pure iron, pure nickel and pure copper. Diffusion coefficients are given at 298 K and solubilities at 623 K and at a hydrogen partial pressure of 1 bar.**

	$\alpha$ -Fe	Ni	Cu
$D_{298\text{K}}$ ( $\text{cm}^2/\text{s}$ )	$9.6 \cdot 10^{-5}$ [18]	$5.3 \cdot 10^{-10}$ [18,35]	$6.3 \cdot 10^{-8}$ [36]
$S_{623\text{K}/1 \text{ bar}}$ (wt.ppm)	$1.3 \cdot 10^{-1}$ [18]	3.3 [18]	$3.3 \cdot 10^{-3}$ [37]

**Table 3 – Chemical composition of the Watt's bath.**

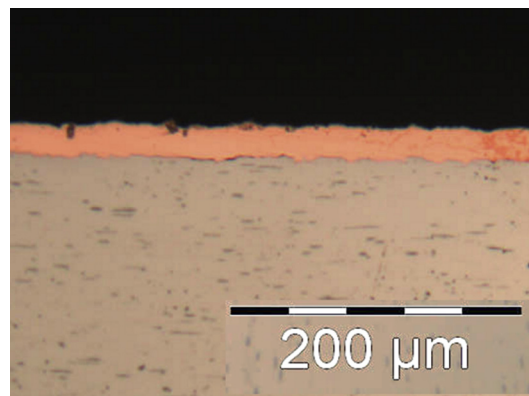
	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	$\text{H}_3\text{BO}_3$
Concentration	280 g/L	65 g/L	45 g/L

**Table 4 – Chemical compositions of the copper sulphate baths.**

	$\text{CuSO}_4$	$\text{H}_2\text{SO}_4$
Concentration of the Cu pre-deposition bath	110 g/L	240 g/L
Concentration of the Cu deposition bath	250 g/L	30 g/L

Ni electrodepositions are realized in a Watt's bath [22,23] whose chemical composition is given in Table 3, with a current density of 6  $\text{A}/\text{dm}^2$  at 55  $^\circ\text{C}$ , and with a pH equal to 4.0. The Cu electrodepositions are realized in two sulphate baths [24,25] successively, the first one ensuring the adherence of the deposit on the substrate with a first 1  $\mu\text{m}$  thick layer. Their chemical compositions are the only difference and are given in Table 4. The temperature is kept at 30  $^\circ\text{C}$  and the applied current density is 2  $\text{A}/\text{dm}^2$ . The thickness of all the electrodeposited layers is controlled with a Fischerscope Xan X-Ray<sup>®</sup> Fluorescence device and kept between 25  $\mu\text{m}$  and 30  $\mu\text{m}$  (Fig. 1). A good adherence of the electrodeposited layers on the substrates is observed (Fig. 1).

The hydrogenation of the tensile tests samples and of the corresponding hydrogen titration samples is realized in an autoclave, under an atmosphere of gaseous hydrogen of 99.99% purity, at 723 K and 200 bars during 48 h. The samples that are used as references, and that are not hydrogenated, are annealed at 723 K during 48 h under vacuum, after electroplating if necessary. At the end of the hydrogenation, about 3 min are required to open the autoclave while the hydrogen pressure is cut, and to quench the specimen in water before storing them in liquid nitrogen. Since the temperature of the samples is still high, hydrogen desorption is promoted between the opening of the autoclave and the quenching. Before testing, hydrogenated and reference samples are stored in liquid nitrogen.

**Fig. 1 – Cross section of a Cu electrodeposited layer on a ferritic steel substrate.**

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