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New High Concentration-High Temperature Hydrogenation Method for Slow Strain Rate Tensile Tests

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Abstract

The aim of the present paper is to propose an innovative hydrogenation method based on metal hydride dissociation.

By heating metal hydride, high pressure of molecular hydrogen is generated, which can be used to promote diffusion through the steel, resulting in very high atomic hydrogen concentration.

This new hydrogenation method was tested on a F82H steel, a Reduced Activation Ferritic/Martensitic (RAFM) steel developed for nuclear fusion application, where high temperature Hydrogen Embrittlement (HE) is a matter of serious concern.

The main goal of this study is to propose a methodology to perform tensile tests on steel at high temperature and high hydrogen contents.

The technique is easy and cheap. Furthermore, by using different metal hydrides and tuning temperature, different hydrogen concentration can be tested.

Key words: Hydrogen Embrittlement. Hydrogenation. F82H steel. Metal Hydride. SSRT test.

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1 Introduction

Hydrogen in steel is known to be very harmful with respect to mechanical properties, in particular ductility [1–4].

Slow Strain Rate Tensile ($SSRT$) tests (strain rate of about $10^{-7} \div 10^{-5}\ s^{-1}$ [1,5]) are usually performed to analyze hydrogen embrittlement effects. It is because the HE phenomena is governed by the time that hydrogen needs to move towards crack formation sites.

HE susceptibility is also temperature dependent. There are many high temperature applications where steels can experience hydrogen absorption. In all these applications, measuring the HE susceptibility, e.g. by SSRT tests, is fundamental in order to determine stress limits related to hydrogen content.

There are two different routines to perform tensile test on hydrogen charged specimens:

- hydrogen charging before the test,
- hydrogen charging during the test.

The first method can not be used for high temperature tests because of hydrogen losses by diffusion during the test. Fig.1 shows calculated hydrogen losses for F82H kept at different temperatures. Calculations were carried out using both the diffusivity data measured by high temperature gaseous permeation tests [6], and the geometry aspect of the $ASTM$ specimen [7].

Hydrogen loss become detrimental for temperature higher than $150 \div 200$ °C. For a test temperature of 200 °C, hydrogen content becomes one half of its initial value after about 20 minutes. As SSRT duration is 0.5 to 2 hours for ASTM specimens, therefore it is not possible to perform SSRT on previously charged specimen at these temperature (see Fig.1).

Therefore, it is necessary to perform hydrogen charging during the test.

Typically, there are two different possibilities:

- electrochemical charging,
- gaseous charging.

Each of the above mentioned methods has its limitations. Electrochemical charging can not be used for tests performed at temperature higher than 90-95 °C in aqueous solutions, or about twice for brine. In case of gaseous charging, it is necessary to use very high hydrogen gas pressure to obtain high hydrogen concentration, which may induce both safety and operational hazard.

The maximum hydrogen concentration obtained in previous work using electrochemical charging for F82H steel is around 6.3 wppm [1]. Although this value is quite high, it is going to be lost at higher temperature. Furthermore,
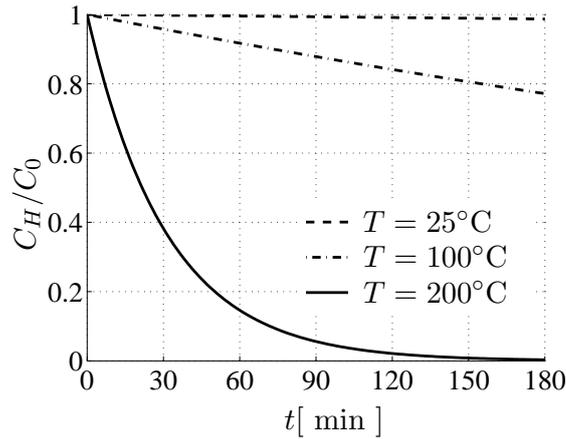
Fig. 1. Hydrogen losses during high temperature SSRT on ASTM F82H specimen.

hydrogen concentration needed to induce HE in steel, increases with increasing temperature. Thus it is not possible to perform tests at high temperature and high hydrogen concentration by means of electrochemical charging only. An innovative hydrogen charging methodology including a novel specimen design is proposed here to overcome these problems.

A hollow cylindrical specimen with an innovative charging mechanism is proposed as an alternative system for high temperature hydrogen charging as shown in Fig.2.
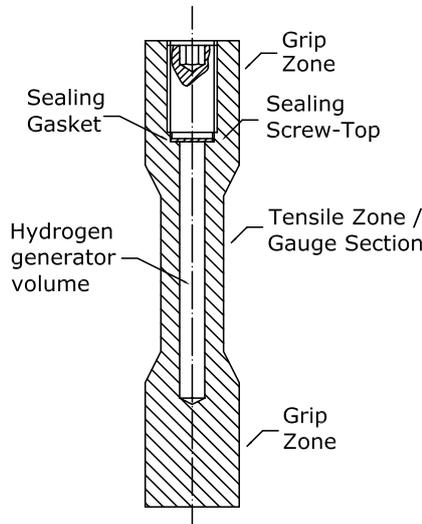

Fig. 2. Schematic representation of the specimen design.

Hydrogen gas is generated by hydride dissociation at high temperature, producing very high hydrogen pressure.

Safety problems related to high hydrogen gas pressure are overcame as the volume involved is very small. Moreover, stresses induced by hydrogen pres-

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sure are not enough to produce materials failure. In any case, they can be considered during data analysis.

The experimental activity of this research is limited to hydrogen charging feasibility.

2 Materials and methods

2.1 Hydrogen generation by means of hydride dissociation

Magnesium hydride has been used as hydrogen generator because it is easily available. Hydrogen is produced through the following reaction:

$$MgH_2(s) \leftrightarrow Mg(s) + H_2(g) \qquad (1)$$

In Fig.3 equilibrium hydrogen partial pressure, P_{H_2}, is reported *vs* temperature, T. As seen from the figure, very high partial pressure can be reached.
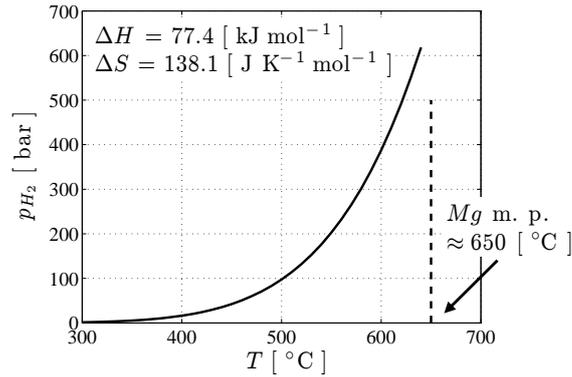

Fig. 3. Equilibrium hydrogen gas pressure for magnesium hydride [8].

Hydrogen partial pressure is only temperature dependent if hydride quantity, stored in the specimen cavity, is enough to keep the metal hydride undissociated up to the end of the test.

Internal volume is designed to contain a little quantity of metal hydride, nevertheless the required hydrogen is slight, also considering the loss by diffusion through specimen walls, for the entire time of the test.

2.2 Model for hydrogen concentration prediction

It is necessary to know hydrogen concentration in the specimen to relate tensile test results to temperature and hydrogen content. Fick's diffusion law is

applied to predict hydrogen distribution across the specimen wall.

Fick's equation was solved in cylindrical geometries [9–11], in order to find hydrogen concentration, C, as a function of radial position, r, and the time, t ($C=C(r,t)$).

At high temperature (more than 200 °C), trap sites can be considered reversible, therefore it is possible to use the local equilibrium hypothesis developed by Oriani [3].

Based on this assumption, effective diffusion coefficient, D_e, was used in order to take into account the trapping mechanism,

$$D_e = D\frac{1}{1 + K\frac{N_T}{N_L}} \tag{2}$$

where D is the Diffusion coefficient, $K = \frac{a_T}{a_L}$ is the ratio between the activity coefficients of hydrogen in traps and in lattice respectively, while N_T and N_L are number of trap sites and lattice sites per unit of volume.

Moreover, by assuming that transient time is relatively short in comparison to the test duration, the time derivative can be neglected. Therefore, cylindrical coordinate diffusion equation becomes

$$\frac{\mathrm{d}^2 C}{\mathrm{d}^2 r} + \frac{1}{r}\frac{\mathrm{d}C}{\mathrm{d}r} = 0 \tag{3}$$

Solution found is

$$C(r) = \frac{C(R_e)\ln\dfrac{r}{R_i} - C(R_i)\ln\dfrac{r}{R_e}}{\ln\dfrac{R_e}{R_i}} \tag{4}$$

where $C(R_i)$, $C(R_e)$ are concentrations of hydrogen in steel at inner radius and external radius respectively.
To simplify $C(R_i)$, $C(R_e)$ can be the equilibrium concentrations given by the Sieverts equation, Eq.6.

$$
\begin{aligned}
C(R_i) &= C_0\sqrt{\frac{p_{H_2}^i}{p_0}}\,e^{-\dfrac{\Delta H_S}{RT}} \\
C(R_e) &= C_0\sqrt{\frac{p_{H_2}^e}{p_0}}\,e^{-\dfrac{\Delta H_S}{RT}}
\end{aligned}
\tag{5}
$$

which are function of molecular hydrogen pressure internal $p_{H_2}^i$ and external $p_{H_2}^e \approx 0$ (so, $C(R_e) \approx 0$). With this assumption neither diffusion coefficient D, or D_e do not play any role.

2.3 Experimental solubility test

Solubility tests at high temperature were performed on F82H steel to verify the efficacy of this charging method. The chemical composition of F82H steel is reported in Tab.1.

Material	C	Cr	Ni	Mo	V	Nb	Si	Mn	S	P	B
F82H	0.09	7.68	0.02	0.003	0.16	0 0.11	0.11	0.002	0.002	0.0002	0.007

Table 1
Chemical composition of F82H steel (in [wt%]).

A scheme of the equipment used for solubility test is shown in Fig.4.
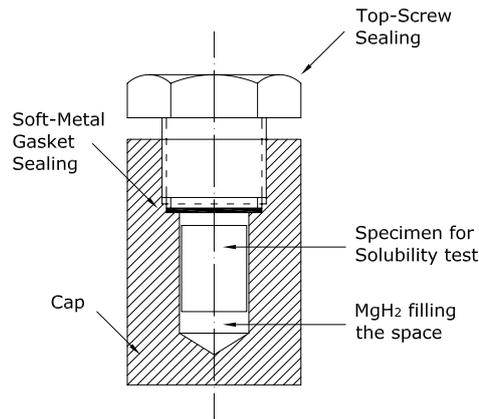

Fig. 4. Hydrogen charging method equipment, based on hydride utilization, for F82H steel.

A F82H cylinder (4 mm diameter, 10 mm height) was inserted in a hollow cylinder together with few milligrams of MgH_2. In order to limit hydrogen losses through the screw, a copper gasket was applied between the opening side and the top-screw. Thanks to copper FCC lattice structure low diffusion loss is guaranteed. Furthermore, as copper has a thermal expansion coefficient higher than steel, the 'o'-ring-metal coupling increases at high temperature, resulting in better sealing.
The cylinder was inserted in a temperature controlled furnace for the time necessary to obtain uniform H concentration across the sample, then the F82H cylinder was water-cooled in order to limit hydrogen losses during cooling.
Measures were performed at different temperature ranging from 300 °C to 700 °C.

Hydrogen content was measured using a degassing system equipped with a thermo-conductibility hydrogen sensor. Sample was heated again to 600 °C for 30 minutes in order to induce the H diffusion. The integral of sensor signal is proportional to total hydrogen quantity previously contained in the sample [6].

3   Results and discussion

In Fig.5 hydrogen concentration data obtained at different temperature are shown. Maximum hydrogen concentration obtained by authors [6] using elec-
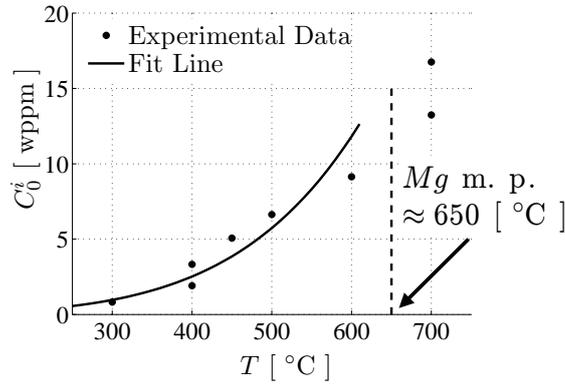

Fig. 5. Experimental hydrogen concentration by MgH_2 production inside F82H steel. Remarkable high H concentration was found.

trochemical method was 6.3 wppm which is much less than maximum value obtained using this new hydrogenation method. Furthermore, this concentration can not be kept during high temperature tensile tests, as discussed before. Concentration data were fitted using a Sieverts law [10,3]:

$$S(p_{H_2}, T) = C_0 \sqrt{\frac{p_{H_2}}{p_0}} \, e^{-\frac{\Delta H_S}{RT}} \tag{6}$$

The maximum hydrogen concentration found was about 15 wppm at 700 °C. It is worthy of note that high temperature data were scattered, which can be explained considering the particular hydride used. Magnesium hydride dissociates to produce metallic magnesium, which has low melting point, therefore, high temperature tests (higher than 650 °C) are not to be related to the temperature itself altered by magnesium adhesion on sample surface. SEM/XRD microanalysis confirmed this fact as a magnesium layer was detected on the specimen surface (Fig.6).
This layer alters the hydrogen absorption in steel and consequently the final hydrogen concentration.
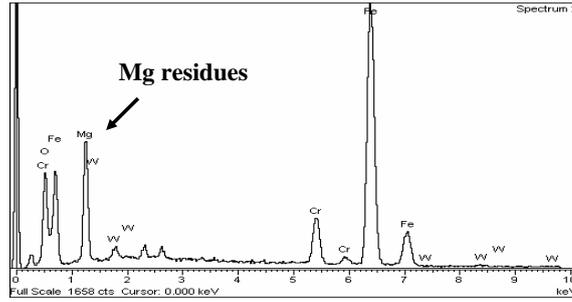
Fig. 6. Mg residues detected on the specimen surface after high temperature charging test.

Moreover, at temperature higher than Mg melting point the phase diagram of $Mg - H$ system presents only liquid Mg and gaseous hydrogen [12], and the thermodynamic equilibrium between the hydride and hydrogen is eliminated. Then for a given temperature the actual H_2 pressure is related to the initial hydride content in the hollow volume of the specimen and this reduces the possibility to relate the hydrogen content, during the mechanical test, to the temperature only. This fact is highlighted by the difference between data at 700 °C in Fig.5.
In order to overcome these problems, a high melting point metal based hydride such as $LaNi_5$ hydride can be used.

Hydrogen distribution in tensile specimen can be determine along radial co-ordinate, according to both the model previously presented (section 2.2) and the measured solubility data. Results are shown in Fig.7.
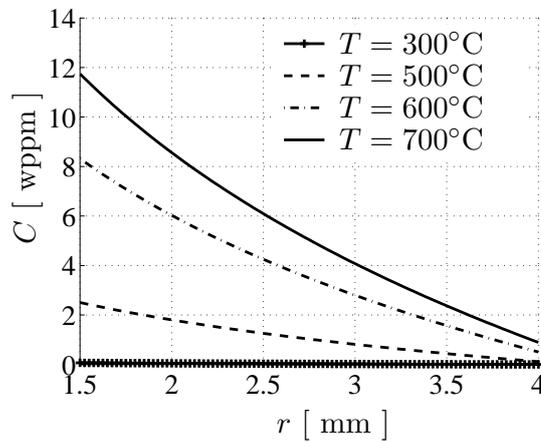

Fig. 7. Concentration distribution in steady conditions through the Specimen wall, at different temperature.

A strong concentration gradient across the wall thickness is inevitable, however, since material experiences embrittlement, tensile tests are supposed to be dominated by the highest hydrogen concentration along the specimen.
Moreover, the use of electroless nickel plating on external surface could act as

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hydrogen diffusion barrier, hence increasing the external hydrogen concentration.

In order to obtain different hydrogen concentrations at a particular temperature, different metal hydrides can be used, with different equilibrium hydrogen gas pressure.

Fig.8 shows the equilibrium hydrogen gas pressure for $LaNi_5 - H$ with respect to MgH_2. A wide pressure range can be obtained by only varying the hydride type.
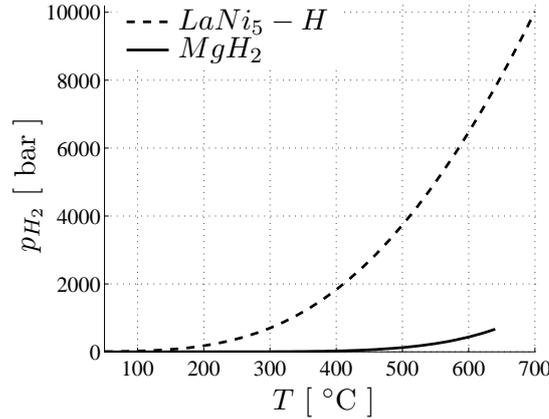

Fig. 8. Comparison between hydrogen pressure produced by $LaNi_5 - H$ hydride and MgH_2 hydride at different temperature.

The very high value of hydrogen pressure, deduced from Ref.[13], need experimental validation since a large extrapolation on temperature was applied.

4 Conclusions

A new high temperature hydrogenation method for steel has been set to be applied in high temperature SSRT tests.

Experimental solubility tests conducted with MgH_2 on $F82H$ steel confirmed the possibility to reach significantly high hydrogen concentrations (up to 15 wppm) at elevated temperature without any hazard. Conventional hydrogenation methods are revealed inadequate for this purpose.

Moreover, this new hydrogenation method has great potential application in high temperature SSRT tests as the hydrogen concentration in the specimen's wall remains constant for longer time than that required for the test. The paper also propose a new specimen geometry suitable for high temperature, high hydrogen concentration Slow Strain Rate Tensile tests.

Theoretical analysis showed that different hydrogen concentrations can be achieved using different metal hydrides and temperatures.

References

[1] M.Beghini, G.Benamati, L.Bertini, I.Ricapito, and R.Valentini. Effect of hydrogen on the ductility reduction of F82H martensitic steel after different heat treatments. *Journal of Nuclear Materials*, 288(1):1–6, 2001.

[2] M.Beghini, G.Benamati, L.Bertini, and R.Valentini. Effect of hydrogen on tensile properties of martensitic steels for fusion application. *Journal of Nuclear Materials*, 258-263(2):1295–1299, 1998.

[3] R.A.Oriani, J.P.Hirth, and M.Smialowsky. *Hydrogen degradation of ferrous alloys*. Noyes publications, 1985.

[4] J. P. Hirt. Effects of hydrogen on the properties of iron and steel. *Metallurgical Transactions*, 11A(6):861–890, 1980.

[5] L.Liu, C.Zhai, C.Lu, W.Ding, A.Hirose, and K. F. Kobayashi. Study of the effect of δ phase on hydrogen embrittlement of inconel 718 by notch tensile tests. *Corrosion Science*, 47(2):355–367, 2005.

[6] G.F.Lovicu. *Hydrogen degradation on nuclear fusion steels*. PhD thesis, University of Pisa, 2005.

[7] ASTM. Hydrogen embrittlement testing. Technical Report ASTM STP 543, American Society for Testing and Materials, 1974.

[8] K.J. Gross and P. Spatz and A. Zuttel and L. Schlapbach. Mechanically milled Mg composites for hydrogen storage the transition to a steady state composition. *Journal of Alloys and Compounds*, 240(1-2):206–213, 1996.

[9] J.Crank. *The Mathematics of Diffusion*. Mathematics in Science and Engineering, 2nd edition, 1975.

[10] R.J.Borg and G.J.Dienes. *Solid State Diffusion*. Academic Press, Inc., 1988.

[11] P.Shewmon. *Diffusion in Solids*. The Minerals, Metals and Material Society, 2nd edition, 1989.

[12] K. Zeng, T. Klassen, W. Oelerich, and R. Bormann. Critical assessment and thermodynamic modeling of the Mg–H system. *International Journal of Hydrogen Energy*, 24(10):989–1004, 1999.

[13] K.H.J. Buschow, P.C.P. Bouten, and A.R. Miedema. Hydrides formed from intermetallic compounds of two transition metals: a special class of ternary alloys. *Reports on Progress in Physics*, 45(9):937–1039, 1982.