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Letter to the Editor

# Fracture toughness of the hydrogen charged EUROFER 97 RAFM steel at room temperature and 120 °C

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ABSTRACT

The static fracture toughness of EUROFER 97 reduced activation ferritic-martensitic steel was investigated in presence of higher content of hydrogen. The hydrogen effect is shown during fracture toughness testing both of base and weld metals at room temperature and at 120 °C. At the room temperature testing the $J_{0.2}$ integral values will decrease depending on hydrogen content in the range of 2–4 wppm. The same hydrogen content of 2 wppm manifests itself by an uneven level of hydrogen embrittlement for base metal and weld metal. This corresponds to a different $J_{0.2}$ integral value and a different mechanism of fracture mode. At the hydrogen content of 4 wppm more evident decrease of $J_{0.2}$ was observed for both metals. At 120 °C hydrogen decreases $J_{0.2}$ integral in base metal at a limited scale only in comparison to weld metal. At room temperature and hydrogen content of about 4 wppm the base metal specimen exhibits inter-granular fracture and trans-granular cleavage on practically the whole crack surface. The weld metal fracture has shown inter-granular and trans-granular mechanism with ductile and dimple rupture.



## 1. Introduction

Reduced activation ferritic-martensitic steels will be used for structural components of the test blanket module (TBM) in the ITER fusion reactor. These steels are potential materials for first wall and blanket structures of demonstration fusion reactor DEMO. In plasma facing materials exposure to higher energy neutrons results in transmutation reactions generating hydrogen and helium. The main source of hydrogen production is a transmutation reaction, e.g. $(n, p)$ in structural materials and hydrogen ingress into material from external sources [1,2]. Significant external sources include hydrogen isotope implementation from plasma side as well as tritium permeation from breeder material into the TBM structure. The increase of hydrogen content and its diffusivity can influence the degradation of mechanical and fracture properties and leads to hydrogen embrittlement. Therefore the effects of hydrogen on fracture toughness of TBM structure materials have to be considered and evaluated. It was the goal of the present work to investigate the influence of hydrogen charging on static fracture toughness of EUROFER 97 steel.

## 2. Interaction of hydrogen with steel

For TBM components of the helium cooled lithium lead (HCLL) fusion reactor prototype EUROFER reduced activation ferritic-martensitic steel [3] will be used taking into account the operating conditions. This steel shows acceptable properties at higher temperatures and is designed for first wall and blanket structures with regard to its lower corrosion in liquid metals (Pb–Li), stability against swelling and helium embrittlement.

One of the main problems of using this type of steels can be hydrogen embrittlement affected by hydrogen uptake, leading to subsequent degradation of mechanical and fracture properties. The hydrogen creation in candidate materials due to transmutation reactions depends on irradiation conditions and occurs in plasma facing materials as well as in breeding blanket components. It can amount to about 0.9 wppm/dpa for neutron radiation at 14 MeV [4]. The total hydrogen content in steels depends also on other parameters such as diffusivity, permeability, trapping site concentration and distribution as well as on the presence of alloying elements. The hydrogen embrittlement is affected by temperatures and can be substantially lower above 300 °C as a result of increased diffusivity and lower number of trapping sites due to their recovery. At lower temperatures approximately below 200 °C, the hydrogen content and diffusivity are significantly dependent on the presence of trapping sites, such as inclusions, precipitates, grain boundaries, dislocations and microcracks [5,6]. Generally, the uptake of hydrogen in ferritic and martensitic steels is lower and, on the contrary, its diffusion higher, in comparison to austenitic steels.

The effect of hydrogen on structural materials is usually investigated after hydrogen electrolytic charging or, in some cases, after charging in hydrogen atmosphere under high pressure and tem-

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perature. The published results of experiments with ferritic-martensitic steels show that hydrogen cathodic charging could take place both under low current density lasting even several days (4 mA/cm$^2$ for 72 h [3]) and higher current densities for a shorter period of time (above 10 mA/cm$^2$ for several hours [7]). These methods enabled hydrogen concentration in the sample to reach up to ~8 wppm.

## 3. Experimental

EUROFER 97 steel plates of thickness 14 mm were heat treated: hardening 980 °C/27 min/air, tempering 760 °C/90 min/air. A weld joint was prepared from two plates 14 × 90 × 300 mm by the TIG method with EUROFER filler wire of Ø 1 mm in the CEA Saclay [8]. Weld heat treatment was performed at 740 °C for 2 h 30 min. Material chemical composition is given in Table 1.

The testing was performed with KLST specimens of 3 × 4 × 27 mm (Fig. 1) machined from plates and weld joint with notch orientation parallel to rolling direction. Specimens were side grooved and pre-cracked before hydrogen charging. Depth of the side groove was 0.2 mm and radius 0.25 mm, pre-crack was produced by high cycle loading.

KLST specimens were cathodic charged for 2 h in 0.5 M $H_2SO_4$ solution with the addition of 0.5 g/l $NaAsO_2$ as hydrogen recombination poison. For KLST specimens, the period of 2 h, current density of 5 and 150 mA/cm$^2$ and the temperature of 75 °C were chosen as optimum parameters. After charging the specimens were stored in liquid nitrogen until the tests of fracture toughness were started. After testing, one half of the specimens were kept in liquid nitrogen before hydrogen analysis was performed. Hydrogen content prior and after testing was analyzed with LECO RH 404 by inert gas fusion, hot extraction and gas mixture thermal conductivity measurement. The error of measurement was ±0.1 ppm.

The three-point bend method, the compliance method as well as the Instron 1342 tensile testing machine were used for measurements. The critical value of *J*-integral $J_{0.2}$ has been evaluated. *J*-integral experimental points and crack growth values of *JR* curve were adjusted by a power regression curve and $J_{0.2}$ values were measured at the point of intersection of *J–R* curve and 0.2 mm exclusion line. A detailed description of the method is given in ASTM E1820-01. $J_{IC}$ and $K_{IC}$ values have not been determined because the validity of measurement was not met due to small specimen sizes. $J_{0.2}$ value was determined from measurements of twelve KLST specimens at room temperature (RT) and 120 °C. KLST specimen testing took no more than approximately 1 h. Parameters of hydrogen charging and testing for fracture toughness are given in Table 2. The hydrogen content analyzed after testing was used for fracture toughness evaluations.

## 4. Results

EUROFER 97 in as-received condition contains 0.3–0.4 wppm of hydrogen. Hydrogen content increases with current density of charging up to 4 wppm of base metal and 8 wppm of weld metal. Hydrogen content (wppm) vs. current density $i_C$ [mA/cm$^2$] for the 2 h charging is given in Fig. 2. The relation of $C_H$ vs. $i_c$ for base metal and weld metals can be described in Eq. (1) for base metal and in Eq. (2) for weld metal:

**Table 1**
Chemical composition of EUROFER 97 (wt%).

| C | Mn | Si | P | S | Cr | V | W | Ta | Ni |
|---|---|---|---|---|---|---|---|---|---|
| 0.11 | 0.47 | 0.040 | 0.005 | 0.004 | 8.82 | 0.20 | 1.09 | 0.13 | 0.022 |

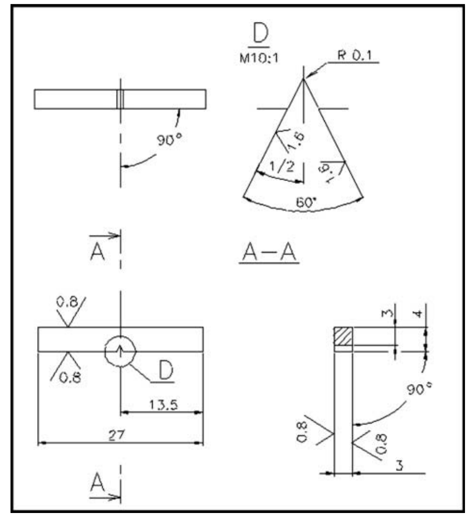


**Fig. 1.** KLST specimen.

$$C_H[\mathrm{ppm}] = 0,6844 \ln i_C + 0,5926 \quad \text{base metal} \tag{1}$$

$$C_H[\mathrm{ppm}] = 0,9892 \ln i_C + 2,6524 \quad \text{weld metal} \tag{2}$$

where constants are dependent on charging time, solution and temperature. The conditions of hydrogen trapping in specimens during the tests were evaluated by the measurement of hydrogen content versus release time at temperatures of 20, 120 and 150 °C. The results are given in Figs. 3 and 4 for base metal and weld metals. The relations show that there is no hydrogen release during testing at RT, but significant release below 2 wppm was observed for about 1 h at 120 and 150 °C.

The effect of hydrogen on $J_{0.2}$ integral was evaluated as a function of its content after the testing at RT and 120 °C. At room temperature there is a considerable decrease of $J_{0.2}$ integral values of base metal at 2 and 4 wppm, while in case of weld metal it is only at 4 wppm, as given in Fig. 5.

For base metal, the $J_{0.2}$ 420 KJm$^{-2}$ initial value decreases below 100 KJm$^{-2}$ for hydrogen contents of 2 and 4 wppm. For weld metal, the $J_{0.2}$ 390 KJm$^{-2}$ initial value shows a similar decrease only for 4 wppm; a decrease to about 250 KJm$^{-2}$ was observed for 2 wppm.

At the 120 °C testing hydrogen effect manifests itself by the decrease of $J_{0.2}$ integral only in base metal in comparison to weld metal. Measured values are summarized in Fig. 6. The $J_{0.2}$ value of base metal decreases by 30% at hydrogen content of about 1.6 wppm while in weld metal the $J_{0.2}$ value with 1.3 wppm corresponds to the value of an uncharged specimen. It is difficult to evaluate higher hydrogen release in less than 1 h with regard to time needed for specimen heating and other experimental conditions.

With increasing temperature the effect of hydrogen decreases. In Fig. 7 the $J_{0.2}$ integral value of base metal reaches the values of uncharged specimens approximately at 200 °C. For weld metal these conditions are met at temperatures ranging from 100 to 150 °C as given in Fig. 8.

For the assessment of failure mechanism fractographic investigations were carried out. The results of observations are given in Table 3. At the RT testing base metal with 4 wppm has shown inter-granular (IG) fracture and trans-granular (TG) cleavage that was observed on the whole crack growth surface except surface near the final fracture (Fig. 9). In some cases quasi cleavage was indicated in restricted areas. With hydrogen containing 2 wppm and with expanding crack surface, the share of cleavage decreases and ductile dimple (D–D) ruptures in the middle area of the crack increases (Fig. 10).

**Table 2**
Hydrogen charging and fracture toughness testing.

| Metal | H-charging | | | | Fracture toughness | | |
|---|---|---|---|---|---|---|---|
| | Current density (mA/cm$^{-2}$) | Charging time (min) | $H_2$[x] after charging | $H_2$[x] after testing | Number of specimens | Temperature (°C) | Test time (min) |
| Base metal | 10 | 120 | 2.5 | 2–2.5 | 12 | 25 | 20–40 |
| | 150 | 120 | ~4 | ~4 | 12 | 25 | 20–40 |
| | 150 | 120 | ~4 | 1–1.5 | 12 | 120 | 45–100 |
| Weld metal | 5–10 | 10–15 | 2.5 | 2–2.5 | 10 | 25 | 20–40 |
| | 10 | 120 | ~4 | ~4 | 10 | 25 | 20–40 |
| | 150 | 120 | 7–8 | 1–2 | 10 | 120 | 45–100 |

[x] Determined hydrogen content in wppm.

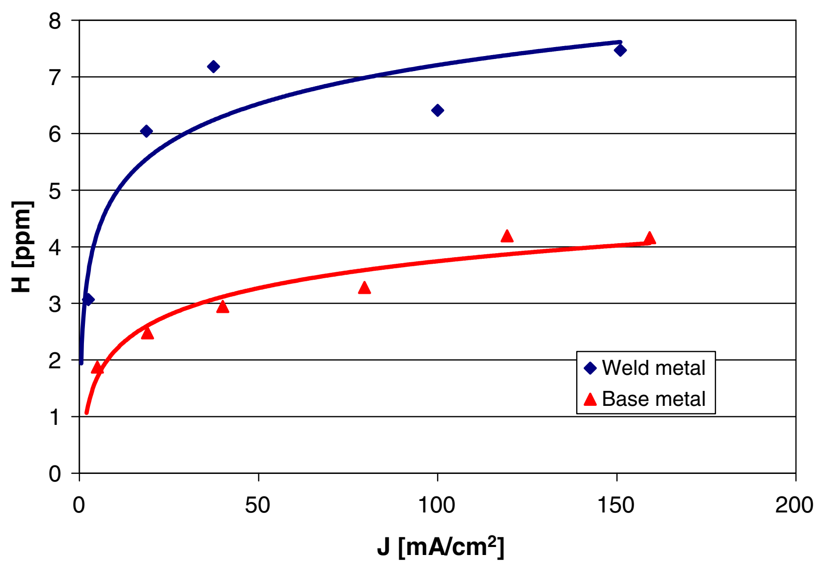


**Fig. 2.** Hydrogen content as a function of current density of electrolytic charging.

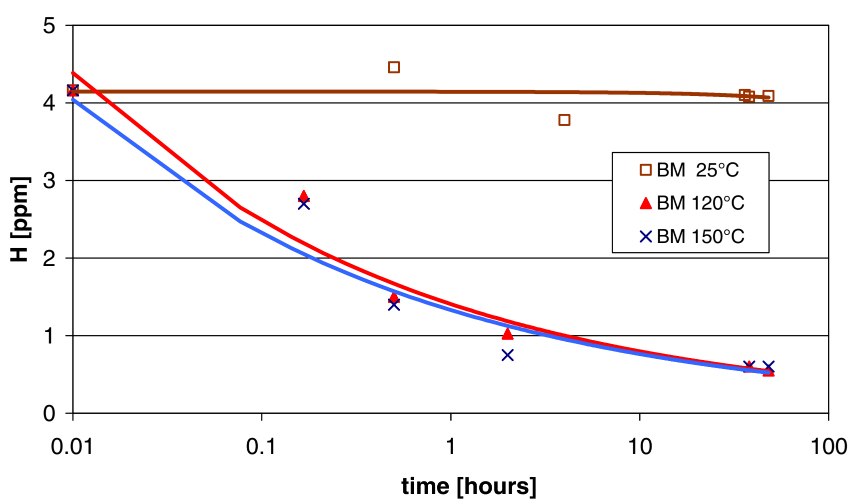


**Fig. 3.** Effect of release time and different temperatures on hydrogen content in EUROFER base metal.

At the RT weld metal with 4 wppm has shown brittle fracture with inter- and trans-granular mechanism. Ductile and dimple ruptures manifest themselves on fracture surfaces in a limited extent. The specimen with 2 wppm exhibits trans-granular cleavage on a very limited area near the pre-crack boundary. At the 120 °C testing ductile and dimple behavior was only observed both on base and weld metal specimens with 1–2 wppm.

## 5. Discussion

The evaluation of results has shown that hydrogen embrittlement is controlled by hydrogen trapping in steel. The susceptibility of EUROFER 97 steel to hydrogen trapping can be evaluated by cathodic charging uptake and hydrogen release. The hydrogen content levels attained were two times higher in weld metal in com-

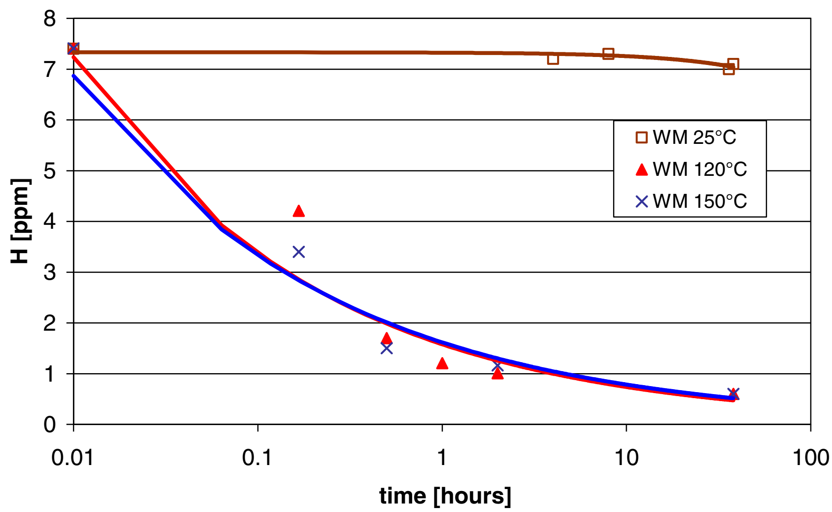


**Fig. 4.** Influence of released time and different temperatures on hydrogen content in EUROFER weld metal.

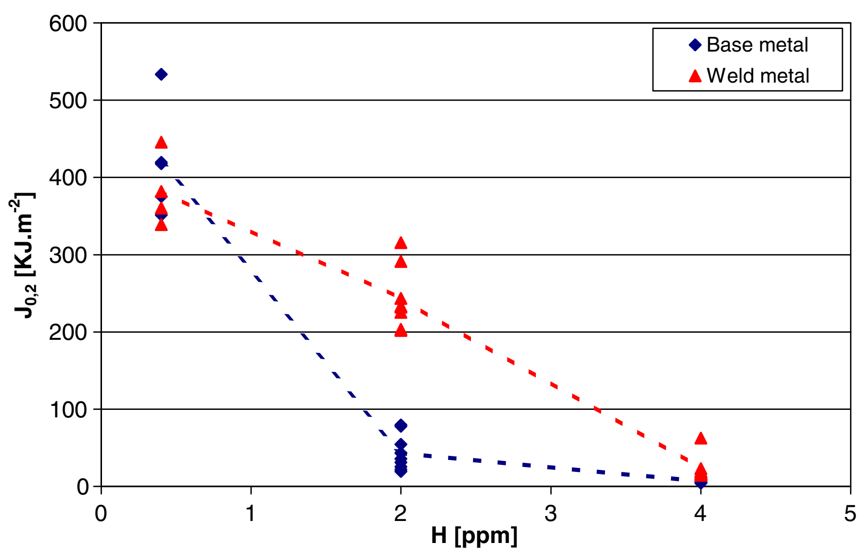


**Fig. 5.** Change of $J_{0.2}$ integral as a function of hydrogen content, testing temperature 25 °C.

parison with base metal after charging in the range of 5–150 mA/cm$^2$ for the same charging time. Hydrogen release has a similar slope both for base metal with up to 4 wppm and for weld metal with up to 8 wppm. These relations show a higher number of trapping sites for hydrogen uptake in weld metal than in base metal. Different values of $J_{0.2}$ integral for the same 2 wppm levels in base and weld metals showed a different level of the embrittlement. The lower effect of hydrogen on weld metal may be the result of lower amount of hydrogen occupied trapping sites, which are not sufficient for achieving the same fracture damage observed in base metal. The following mechanism is probably operating in our testing conditions:

- The same hydrogen content in weld and base metals manifests itself by lower saturation of trapping sites of weld metal in comparison to base metal in which higher trapping site saturation is attained by the same charging conditions as a result of a lower number of microstructural defects.
- The same hydrogen embrittlement for both metals requires higher hydrogen content in weld metal. This enables achieving the required amount of saturated trapping sites in weld metal corresponding base metal conditions and hence the similar extent of brittle mechanism of fracture.
- Density and distribution of trapping sites in the metal matrix can affect hydrogen content and both inter-granular and trans-granular damages as well as ductile rupture during specimen testing.

Hydrogen charging techniques of EUROFER 97 used in this work correspond to the investigations of ferritic and martensitic steels [3,4,7]. Similar to our results, the hydrogen release was observed with 2Cr–1Mo and 3Cr–1Mo-V steels after cathodic and/or gaseous charging. There were no hydrogen changes after keeping at RT for 48 h. Hydrogen content decreased to 0.2–0.4 wppm of the original values at 100 °C after 1 h [9].

Regarding TBM potential materials, ferritic-martensitic steels lose their ductility and plasticity with increased hydrogen content. The hydrogen embrittlement was investigated in terms of tensile properties and fracture toughness measured at RT testing. At the slow strain rate test (SSRT) on F82H (9CrWV) ferritic-martensitic steel embrittlement at 1–2 wppm was observed. The main mechanism was inter-granular fracture [4]. Similarly, hydrogen affects

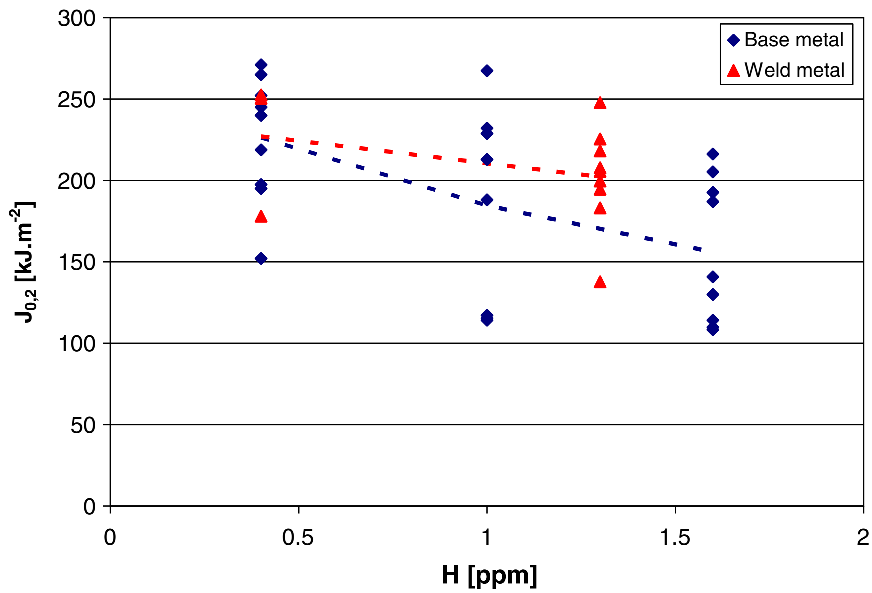


**Fig. 6.** Change of $J_{0.2}$ integral as a function of hydrogen content and testing temperature 120 °C.

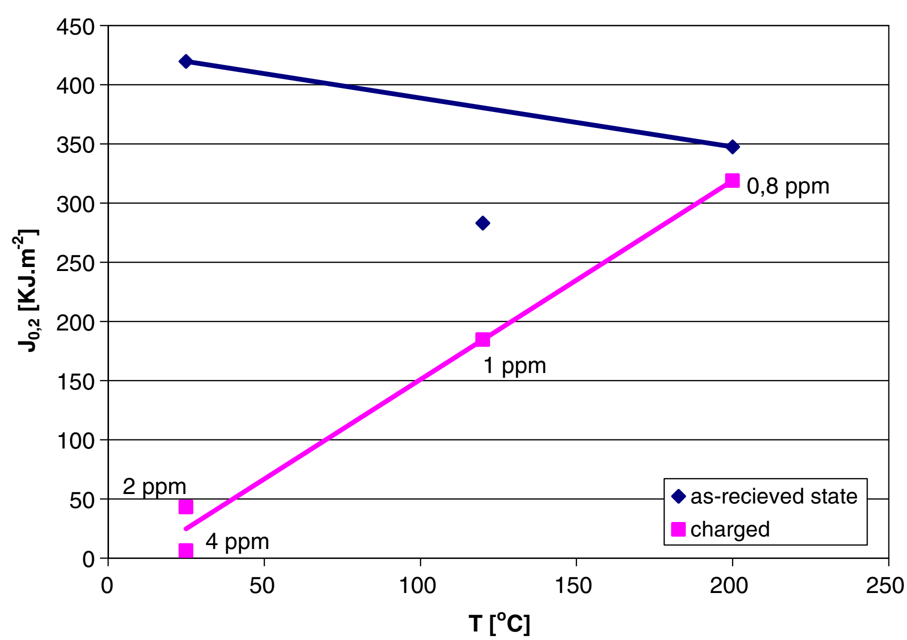


**Fig. 7.** Change of $J_{0.2}$ integral as a function of testing temperature for base metal.

fracture toughness of F82H steel. The 4 wppm content considerably decreased the total critical $J$ values and also reduced the resistance to crack propagation [10].

Hydrogen embrittlement of EUROFER 97 manifests itself at room temperature already with 1–2 wppm content; Maday [3] gives 1.6 wppm. In her work, EUROFER 97 and T 91 (9CrMoVNb) steel investigated by SSRT at dynamic charging showed decreasing of reduction of area at 1.6 wppm and reveals similar inter-granular fracture of both steels. In another work [11] susceptibility of base and weld metals of EUROFER 97 was measured by low cycle fatigue test after charging ranging from 2.5 to 6.5 wppm. A visible fatigue lifetime decrease and inter-granular or trans-granular separation were observed above 5.5 wppm.

To be able to apply the results to the fusion reactor components, it is necessary to consider the effect of hydrogen and radiation embrittlement under conditions important for operational parameters mainly in temperatures ranging from 300 to 550 °C. The number of publications on synergistic effect is limited. Relevant for our assessment are investigations of 9%Cr–2%W reduced activation ferritic- martensitic steel [12], MANET II (10CrWV) and F82H steels[1] as well as low alloy 2.5%CrMoV and 2%CrNiMoV ferritic steels [13,14]. The results obtained with 9%Cr–2%W steel irradiated up to $6 \times 10^{24}$ n/m$^2$ at 300 °C, compared with unirradiated one, reveal a decrease of tensile elongation of with increasing charging current density. Manet II and E82H steels implemented with protons were tensile tested on miniaturized specimens measured at

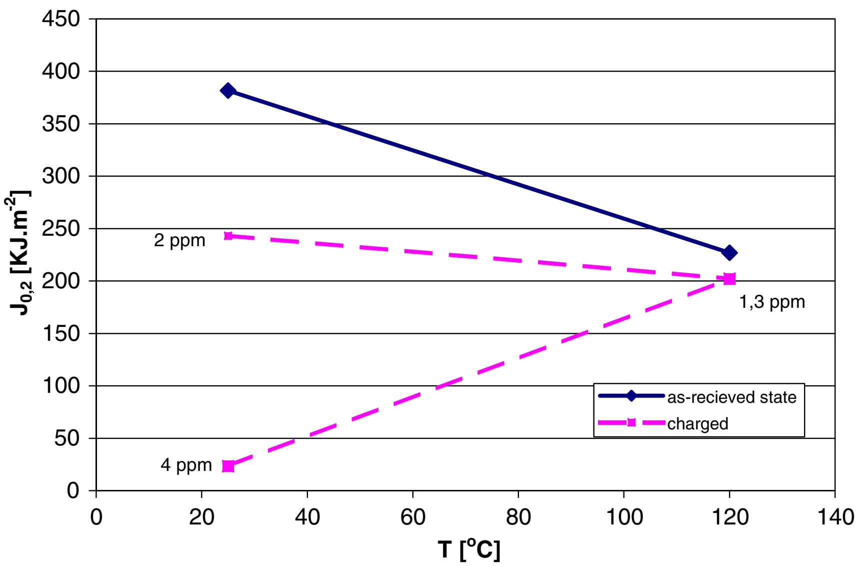


**Fig. 8.** Change of $J_{0.2}$ integral as a function of testing temperature for weld metal.

**Table 3**
Testing conditions and fracture surface mechanism.

| Material | Charging current (mA/cm$^2$) | H initial content (wppm) | H content after test (wppm) | Testing temperature (°C) | Fracture surface | |
|---|---|---|---|---|---|---|
| | | | | | At pre-crack middle area | End of crack |
| Base metal | As-received | 0.35 | | 20 | Ductile–dimple | |
| | 10 | 2.5 | 2–2.5 | 20 | IG and TG | D–D |
| | 100 | 4 | 4 | 20 | IG and TG | D–D |
| | 100 | 4 | 1–1.5 | 120 | Ductile–dimple | |
| Weld metal | As-received | 0.35 | | 20 | Ductile–dimple | |
| | 5 | 2.5 | 2–2.5 | 20 | Ductile–dimple | |
| | 10 | 4 | 4 | 20 | IG, TG, D–D | D–D |
| | 100 | 4 | 1–2 | 120 | Ductile–dimple | |
| | 100 | 6 | 1–2 | 120 | Ductile–dimple | |

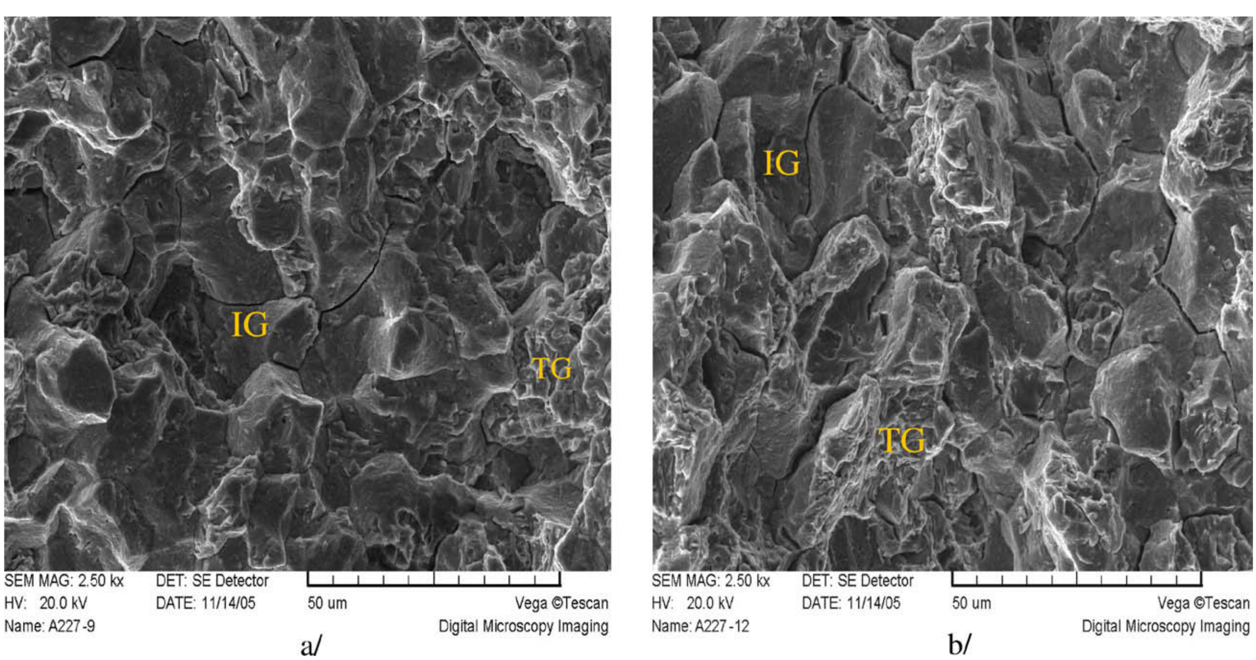


**Fig. 9.** Crack growth fracture surface of base metal specimen, hydrogen content 4 ppm, room temperature testing: (a) area near crack initiation, (b) central area of crack growth surface.

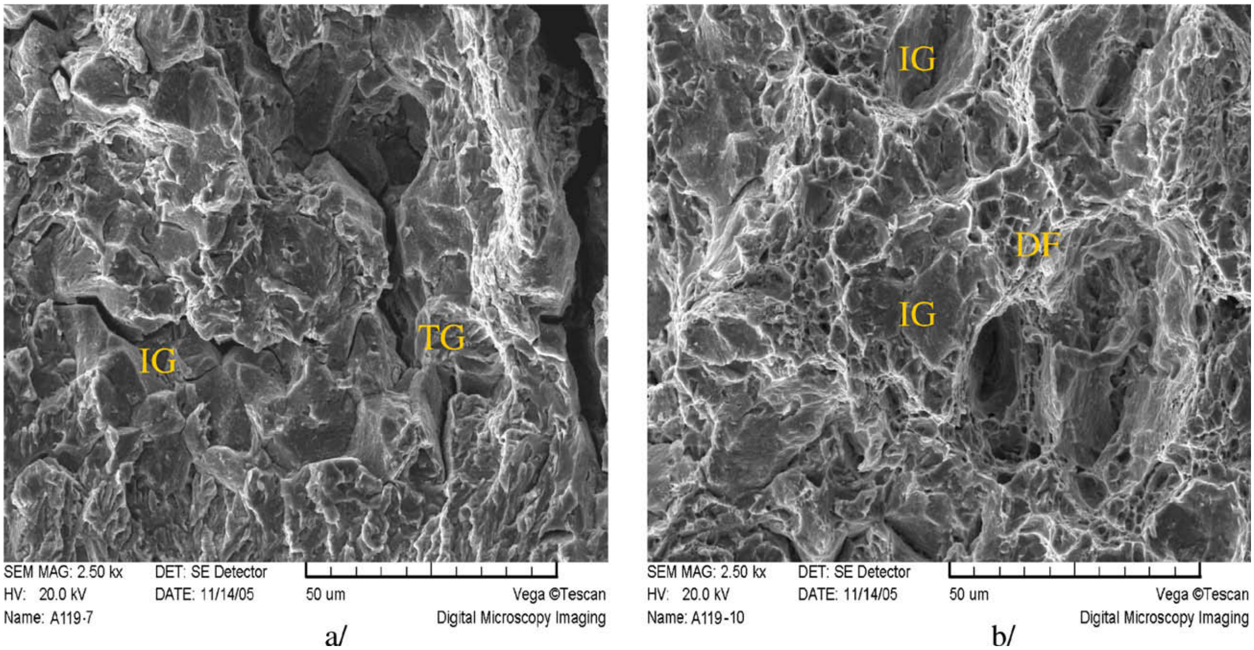


**Fig. 10.** Crack growth fracture surface of base metal specimen, hydrogen content 2 ppm, room temperature testing: (a) area near crack initiation, (b) central area of crack growth surface.

RT and higher temperatures. Slight decrease of ductility at RT took place after implementation below 7 wppm content; practically no effect on elongation was observed at testing temperature of 350 °C. The above mentioned low alloy steels were tested at RT after cathodic charging for 2–10 wppm hydrogen content. They showed similar decrease of ductility and fracture toughness of unirradiated specimens and specimens irradiated with $5-10 \times 10^{23}$ nm$^{-2}$ fluences at 290 °C while tensile specimens irradiated at 130 °C showed considerable loss of plasticity. Both for ferritic-martensitic steels and low alloy steels the critical hydrogen content for brittle fracture initiation reached lower values in case of irradiated specimens.

In general terms, the results of the above given investigations show that degradation under irradiation should significantly manifest itself both at lower temperatures up to 250–300 °C and higher fluences due to higher amount of trapping sites. At temperatures above 300 °C the influence of hydrogen did not manifest itself at all [4,15,16]. There are two competition processes: one between radiation damage and dynamic recovery of irradiation induced defects and second one between hydrogen capture and release due to increased its diffusivity at higher temperatures. The effect of hydrogen in ferritic-martensitic steels will be, compared with austenitic steels, determined by a relatively higher diffusivity and lower solubility that could decrease susceptibility of these steels to hydrogen and radiation embrittlement.

## 6. Conclusions

Base and weld metals of EUROFER 97 testing performed proved fracture toughness susceptibility and brittle fracture depending on the hydrogen content ranging from 2 to 4 wppm. At room temperature the hydrogen content of about 4 wpm decreases $J_{0.2}$ integral both of base and weld metals approx. by 90% of original values. Hydrogen containing 2 wppm manifests itself significantly only in base metal. The reduction of fracture toughness corresponds to the failure mechanism, involving, in case of base metal brittle fracture and in case of weld metal ductile dimple rapture only. At the 120 °C testing the hydrogen affects base metal at a limited scale only.

The available results of fracture/mechanical properties of ferritic and martensitic steels show that hydrogen embrittlement can be observed at lower temperatures up to about 250 °C and 2–8 wppm hydrogen contents and is given by material composition and microstructure, by efficiency of trapping sites, hydrogen diffusivity and release. At higher temperatures, the hydrogen effect will be significantly affected by the higher release and lower content of hydrogen in steels.

It is evident that the experimental conditions differentiate from the operating conditions of the fusion reactor blanket. In this case hydrogen uptake takes place as a result of increased number of irradiation defects and their affinity to hydrogen trapping both affected at higher temperatures. Therefore further works should deal with testing the synergetic effect of hydrogen and irradiation damage on EUROFER reduced activation ferritic-martensitic steel embrittlement.

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