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Water corrosion of F82H-modified in simulated irradiation conditions by heat treatment

J. Lapeña *, F. Blázquez

CIEMAT, Avda. Complutense 22, 28040 Madrid, Spain

Abstract

This paper presents results of testing carried out on F82H in water at 260°C with 2 ppm H_2 and the addition of 0.27 ppm Li in the form of LiOH. Uniform corrosion tests have been carried out on as-received material and on specimens from welded material [TIG and electron beam (EB)]. Stress corrosion cracking (SCC) tests have been carried out in as-received material and in material heat treated to simulate neutron irradiation hardening (1075°C/30′ a.c. and 1040°C/30′ + 625°C/1 h a.c.) with hardness values of 405 and 270 HV30, respectively. Results for uniform corrosion after 2573 h of testing have shown weight losses of about 60 mg/dm^2. Compact tension (CT) specimens from the as-received material tested under constant load have not experienced crack growth. However, in the simulated irradiation conditions for a stress intensity factor between 40 and 80 MPa$\sqrt{m}$, crack growth rates of about 7×10^{-8} m/s have been measured.

1. Introduction

Low-activation ferritic/martensitic steels are considered as structural materials for the fusion reactor DEMO because of resistance to thermal stress and swelling and better resistance against neutron irradiation damage compared with austenitic steels [1–3]. Investigations of some authors [2,4,5] have shown that neutron irradiation at temperatures higher than 350°C produces a rapid hardening in the early stages of displacement damage. Above 20 dpa, irradiation hardening decreases and reaches a saturation level, but significant irradiation hardening has been observed at lower temperatures (200–350°C) and low damage level.

Although mechanical properties with irradiated and unirradiated specimens have been studied, there are not many data available on the corrosion behaviour in water for these steels [6–8], and most of the studies have been focused on uniform corrosion. Taking into account that some parts of these steels will be in contact with water, it is important to know their behaviour in that environment.

In this paper, results of tests carried out in water with additives are presented in order to study the behaviour of the reduced-activation martensitic steel F82H, which is a candidate for the first wall of the fusion reactor DEMO. To simulate the embrittlement effect produced by neutron irradiation, two thermal treatments have been carried out to obtain a hardened material.

Uniform corrosion and stress corrosion crack growth tests have been carried out at 260°C in water with 0.27 ppm of lithium, in order to obtain pH = 7 at 300°C, and 2 ppm of hydrogen at room temperature. Temperature and chemical conditions were agreed on by the Corrosion Group from the Structural Material European Blanket Project.

2. Experimental

2.1. Stress corrosion crack growth test

The material used in this study was the reduced-activation ferritic/martensitic steel F82H modified, heat 9741 (7.65Cr, 2.1W, 0.1C, 0.16Mn, 0.14V, 0.005S, 0.02Ta, wt%, bal. Fe). This steel was supplied as plates in the normalized (1040°C/37′) and tempered (750°C/1 h/a.c.) conditions with a hardness of HV30 = 204.

Two thermal treatments were carried out on two different pieces in order to simulate the embrittlement produced by neutron irradiation: normalization

* Corresponding author. Fax: +34-91 346 6661.
E-mail address: jesus.lg@ciemat.es (J. Lapeña).

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Table 1
Tensile properties

	Yield strength (MPa)		Tensile strength (MPa)		Elongation (%)		R.A. (%)	
	R.T.	260°C	R.T.	260°C	R.T.	260°C	R.T.	260°C
As-received	504	–	618	–	28.4	–	82	–
1040°C/30′ 625°C/1 h	723	657	810	714	16.7	15	76	77
1075°C/30′	847	897	1260	1317	12.6	9.8	56	40

(1075°C/30′/a.c.) and normalization plus tempering (1040°C/30′ + 625°C/1 h/a.c). Hardness values were 405 and 270 HV30, respectively. Mechanical properties for each treatment, as well as in as-received condition, are summarized in Table 1.

As-received material showed a tempered martensitic structure containing large amounts of carbides. They had precipitated preferentially at the prior austenitic grain boundaries and at the lathe boundaries, but also in the bulk or the martensite lathes. No significant differences were observed in the microstructure of the material with intermediate hardness. In the normalized condition, the microstructure consisted of lathe martensite. In all the material conditions, the average prior austenite grain size was ASTM 4.5–5.5.

Fracture mechanics compact tension (CT) specimens with 12 mm thickness were fabricated according with ASTM E399. Specimens were machined from plate in order to obtain the crack propagation in the rolling direction. Prior to the crack growth corrosion tests, all specimens were precracked in air at a frequency of 22 Hz and $R = 0.1$.

Stress corrosion crack growth tests were performed in a recirculated stainless steel autoclave with 7.5 l capacity. Specimens were tested under constant load by means of a lever and dead weight system incorporated to the autoclave, which has the capacity to test eight specimens at the same time. The water temperature was 260°C, with 0.27 ppm of lithium as additive and 2 ppm of hydrogen at room temperature.

At the end of the tests, specimens were broken by fatigue in air and the fracture surface was studied by scanning electron microscopy (SEM).

2.2. Uniform corrosion test

For uniform corrosion testing, two plates of F82H with weldments have been tested. One of them was TIG welded with a narrow gap by Hitachi with F82H filler wire, and the other was electron beam (EB) welded by Mitsubishi Heavy Industry using an I-groove design without filler metal.

Specimens were cut from each plate in rectangular form of 2–3 mm thickness, 13–15 mm width and 50–60 mm length. Some of them were only from the base material and others contained the weld and heat affected zone in the middle of the specimen. The corrosion tests were performed under the same conditions and autoclave as the stress corrosion crack growth tests.

After exposure in the autoclave, some specimens were removed in order to determine the weight loss. All specimens were electrochemically cleaned with CNNa. This treatment permits the removal of the oxides without producing material attack.

3. Results

3.1. Stress corrosion crack growth test

Two specimens of as-received material and thirteen of normalized material have been tested.

The specimens of as-received material did not show any crack growth after 1200 and 3225 h. However, after opening the specimen by fatigue in air, SEM examination revealed some isolated grains near the crack tip (Fig. 1). However, these grains were in the material not exposed to the environment, ahead or the crack tip. Preliminary results seem to indicate a relationship between these grains and a sulfur stress-driven segregation, but AUGER analyses are still in progress to confirm it.

All specimens of normalized material showed large crack growth even in very short periods (≈ 1 mm during 4 h). Some of them broke during the test (in some cases < 12 h), indicating a fracture toughness value between 120 and 133 MPa$\sqrt{}$m. All specimens showed intergranular fracture (Fig. 2).

Fig. 3 shows the crack growth rate (da/dt) versus stress intensity factor (K). Every specimen is represented with its initial and final stress intensity factor. A trend has been estimated taking into account the short test periods. The results seem to indicate a first stage up to 60 MPa$\sqrt{}$m with an increasing crack-growth rate followed by a second stage with a plateau up to at least 80 MPa$\sqrt{}$m. The final region of this plateau, which is at the same time the start of an accelerated increase in the crack growth rate, has not been determined, but in any case the point of fracture is around 120–130 MPa$\sqrt{}$m. Taking into account that these large crack extensions produce an important increase of the stress intensity

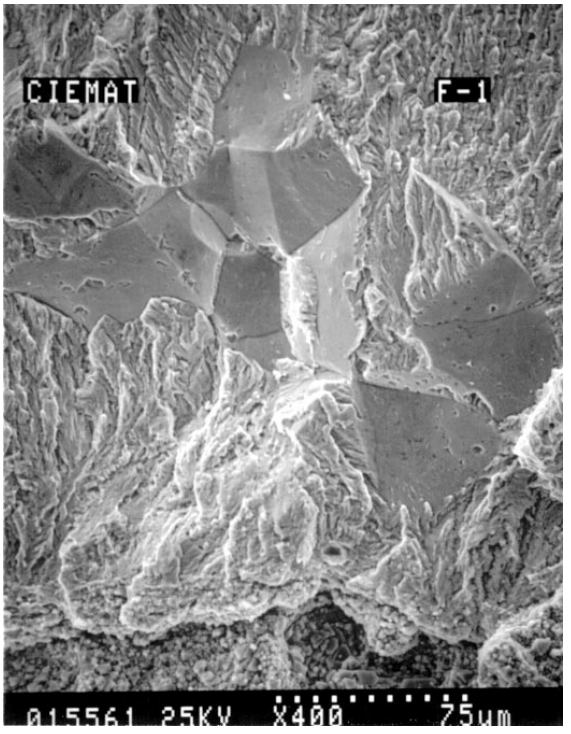

Fig. 1. Fracture surface of CT sample from as-received material after 1200 h.

factor, the crack growth rate will increase from the start to the end of each test except in the plateau region, where da/dt is independent of K. In any case, the lower curve in this figure has been drawn conservatively, taking the average velocity and the final stress intensity factor into account for each specimen.

To determine the influence of hydrogen in stress corrosion cracking (SCC), four specimens have been tested under similar conditions but without hydrogen addition. The crack growth rates obtained are in the same order as the specimens tested with hydrogen (Fig. 3).

One specimen was also tested in an inert atmosphere at the same temperature to be sure that the rapid crack growth was not due to mechanical reasons. After 72 h, no crack growth was detected.

The test with intermediate hardness specimens is in progress. One of the specimens has been examined after 1000 h of testing, and no crack growth has been detected, but as in the case of as-received material, SEM examination revealed some isolated grains near the crack tip, inside the material.

3.2. Uniform corrosion test

After 2573 h, four extractions have been carried out at various intervals. Results of weight loss versus time

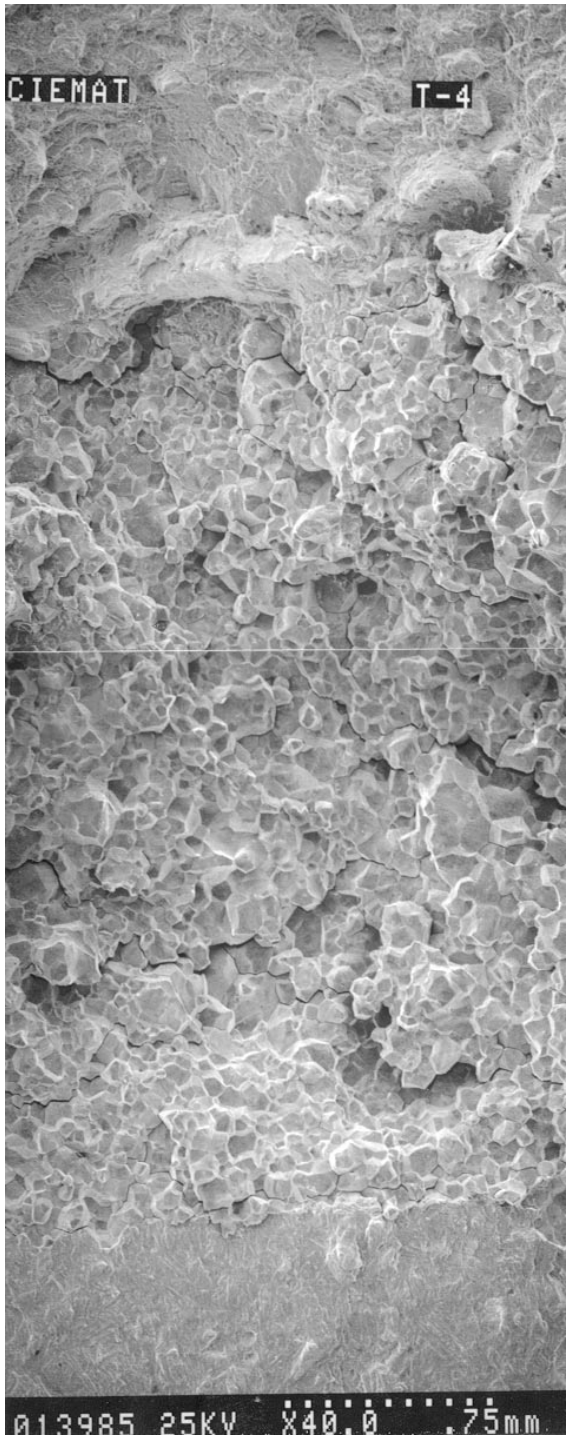

Fig. 2. Fracture surface of CT sample from normalized material after < 12 h.

can be seen in Fig. 4. Weight losses obtained are similar in all specimens, although a little higher in the EB welded material. Testing is in progress and will continue

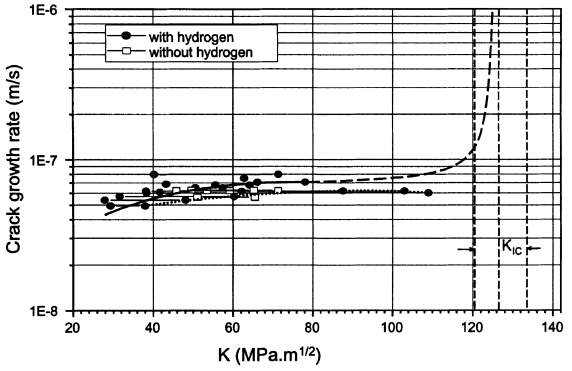

Fig. 3. Crack growth rate versus stress intensity factor for normalized material.

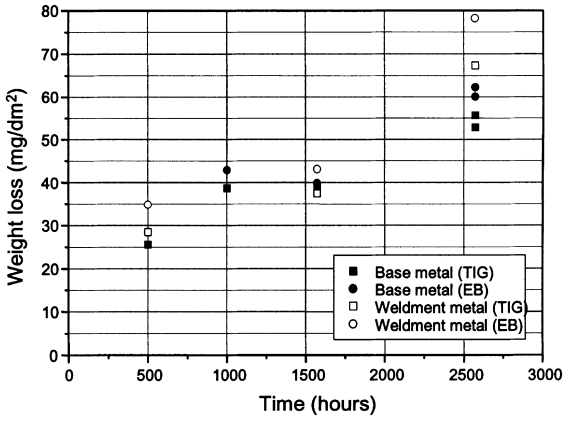

Fig. 4. Weight loss versus time for base and weld material.

up to 5000 h. Quantification of oxide layers and their composition will be determined.

4. Discussion

4.1. Stress corrosion crack growth test

Intergranular stress corrosion cracking (IGSCC) has been observed with a very high crack growth rate in the most hardened material. In other studies of SCC susceptibility of martensitic stainless steels, it was found that a close relationship exists between hardness and SCC susceptibility of the alloys [9,10]. In those studies, IGSCC is produced in materials with a hardness HV > 340 or ultimate tensile strength >1100 MPa, regardless of the alloy specifications.

Although F82H was not studied in the previous works, our results agree with that relation between SCC susceptibility and hardness. The most hardened material (HV = 405, tensile strength = 1317 MPa) experienced IGSCC, but neither the material in the as-received condition (HV = 204, tensile strength = 618 MPa) nor the material with intermediate hardness (HV = 270, tensile strength = 714 MPa) showed SCC susceptibility.

Neutron irradiation at low temperatures (200–350°C) may produce an important hardening. Some results [4] indicate that irradiation of F82H at 3.4 dpa at 325°C produces tensile properties similar to our normalized material. There is a little difference that probably would be compensated if the irradiation was carried out at 260°C. Similarly, irradiation to 3 dpa at 250°C [11] showed a little more hardening than our normalized material. These results seem to indicate that the hardening characteristics of the material tested in the normalized condition could be representative of the hardening produced by some specific neutron irradiation (3–3.5 dpa). However, it is necessary to take into account that the microstructure of the normalized material does not present carbide precipitates while the irradiated material microstructure shows carbides precipitated during tempering.

Although the absence of carbides has a detrimental effect on the corrosion behaviour, a microstructure similar to the one studied in this work could be produced as a consequence of welding process without a proper post-welding heat treatment.

One important effect may be the contribution of hydrogen, which is strongly related to the IGSCC susceptibility. In fact, it is very difficult to distinguish between SCC and hydrogen embrittlement. In our tests, the effect of hydrogen in water was investigated by testing without hydrogen. In both conditions, IGSCC was produced with similar crack growth rates. Some studies [12] indicate that the hydrogen concentration from corrosion at the water–material interface is below 0.04 wppm. One may ask if that hydrogen, which cannot be eliminated, is enough to produce such high crack velocities in a few hours.

The presence of some isolated grains near the crack tip in the material tested in the as-received and normalized-and-tempered conditions may be explained by stress-driven segregation of some elements. Some Auger observations agree with this explanation, but more detailed studies will be made.

4.2. Uniform corrosion test

Weight losses are not very different in all the materials tested. Although weight loss seems a little higher in the EB welded material, more testing time is needed to confirm the preliminary results. Weight losses are about 30 mg/dm^2 at 500 h and 60 mg/dm^2 at 2573 h. The value in reference [13] is 162 mg/dm^2, but this value has been obtained in water with 200 ppb O_2 at 250°C without additives in a 250 h test.

The test is in progress to complete 5000 h, and quantification of oxide layers and their composition will be determined to understand the behaviour of F82H (base metal, weld and heat affected zone) in water at high temperature.

Lithium, as chemical specie, is not expected to play a role in the corrosion behaviour. It was only added to obtain pH = 7 at 300°C.

5. Summary

Uniform corrosion and stress corrosion crack growth tests have been carried out on F82H martensitic steel at 260°C in water with hydrogen and lithium as additive. The crack growth rate tests were made in as-received material and in a hardened condition (normalized and normalized and tempered) to simulate the hardening effect of neutron irradiation. Uniform corrosion tests were carried out on base metal, and TIG and EB weldments.

- IGSCC and high crack growth rates have been measured (about 7×10^{-8} m/s between 40 and 80 MPa$\sqrt{}$m) in the most hardened condition. This condition seems to be representative of neutron irradiation at about 3–3.5 dpa and 260°C, although the material microstructure is different.
- As-received and normalized-and-tempered material is not susceptible to SCC in the condition tested, but some isolated grains have been observed near the crack tip after 1000–1200 h. Auger studies will be completed to confirm whether stress-driven segregation has ocurred at those grain boundaries.
- The SCC susceptibility of F82H in the most hardened condition and its immunity in all the other conditions tested agree with the idea that IGSCC is produced in martensitic steels with a hardness HV >340 or ultimate tensile strength >1100 MPa.
- Weight losses in uniform corrosion tests of 60 mg/dm^2 at 2573 h are a little higher in the EB welded material, but more testing time is needed to confirm these results.

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