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Grain boundary microchemistry and metallurgical characterization of Eurofer'97 after simulated service conditions

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Abstract

The aim of this paper is to describe the microstructural investigations, the mechanical properties (hardness, tensile and charpy) and the grain boundary microchemistry studied by Auger electron spectroscopy (AES), of the Eurofer'97 steel aged in the range of temperatures from 400 to 600 °C up to 10 000 h. After these thermal aging treatments the steel showed a high microstructural stability, and similar values of hardness, ultimate tensile strength and 0.2% proof stress regardless of the material condition. A slight DBTT increase was observed in the material aged at 600 °C for 5000 and 10 000 h. The Auger results showed chromium enrichment at grain boundaries in all material conditions. In addition, phosphorus was detected at the grain boundaries after the aging treatments at 500 °C.
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1. Introduction

At present, the reduced activation ferritic/martensitic steel called Eurofer'97 is the reference structural material for DEMO and for the test blanket modules of ITER. The operating conditions of fusion reactors will be severe [1]. One of the critical issues for judging the acceptability of reduced activation ferritic/martensitic steels for fusion applications is the degradation of properties after long term service at high temperatures [2,3], this problem being strongly dependent on the chemical composition of the steel in addition to service conditions.

In order to evaluate the metallurgical properties (microstructural and mechanical) and the microchemistry at grain boundaries of the Eurofer'97 steel after simulated service conditions, and consequently to evaluate its feasibility as structural material for fusion reactors, in this work the material has been thermally aged at relevant temperatures of the reactor operation.

2. Experimental

The studied material is the reduced activation ferritic/martensitic steel Eurofer'97 (Heat E83698). Its chemical composition (wt%, balance Fe) is: 0.11 C, 8.7 Cr, 1 W, 0.10 Ta, 0.19 V, 0.44 Mn, 0.004 S. The steel was supplied as plates with the following initial metallurgical condition: normalized at 980 °C for 27 min plus tempering at 760 °C for 90 min/air-cooled. In order to investigate the microstructural changes after long-term simulated service at high temperatures and their influence in the mechanical properties, the Eurofer'97 steel was thermally aged at 400, 500 and 600 °C for 1000, 5000 and 10 000 h.

Microstructure was characterized by optical microscopy (OM) and by scanning electron microscopy (SEM). In addition, some TEM investigations of thin foils were performed in a 200 kV JEOL transmission electron microscopy equipped with an X-ray energy dispersive spectrometer (EDS). Also, phase extractions were

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performed by anodic dissolution of the matrix. The identification of second phase precipitates in the extracted residues was performed by EDS (SEM) and by X-ray diffraction (XRD).

The grain boundary microchemistry studies were performed on the Eurofer'97 steel in the as received condition and after aging at 400 °C for 10 000 h, at 500 °C for 1000, 5000 and 10 000 h, and at 600 °C for 5000 h. At least two notched cylindrical samples were studied per condition. Samples were cathodically charged with hydrogen and fractured by tension (deformation rate of 1 μm/sec) inside a PHI660 Scanning Auger Microprobe, at ultrahigh vacuum, with a specially designed fracture stage that allows to analyse the two surfaces obtained after the fracture. Spot analyses were performed on grain boundary facets and on ductile fracture for comparison. Atomic concentrations were calculated according to [4]. Composition depth profiles were obtained using a 2 keV argon ion flux, the etching rate being calibrated with a Ta_2O_5 foil of known thickness.

Vickers hardness measurements (30 kg) were carried out on all aged materials along the three spatial orientations. Tensile tests were also performed in all studied material conditions, using cylindrical specimens of 5 mm diameter and 25 mm of gauge length. The specimens were tested at room temperature and at the same temperature as that of the aging treatment. Charpy impact tests were conducted on material thermally aged at 500 and 600 °C for 5000 and 10 000 h using V-notched specimens according to ASTM Standard E-23. The ductile–brittle-transition-temperature (DBTT) was estimated as 50% brittle fracture mode.

3. Results and discussion

3.1. Microstructural characterization

3.1.1. Optical microscopy and scanning electron microscopy

The microstructure of the Eurofer'97 steel in the as-received condition consisted of tempered martensite with a prior austenite grain size in the range ASTM 10–11.5 (6.7–11 μm) [5]. No significant microstructural changes (prior austenite grain size, morphology, size and distribution of the second phase precipitates) were observed by optical and scanning electron microscopy in any of the aged materials.

3.1.2. Phases extraction and X-ray diffraction

Phase extraction was carried out on all aged materials studied. The results showed that the amount of extracted residue does not change significantly in aged materials (2.5–2.9 at.%) compared to the as-received state (2.5 at.%). This suggests that no significant new nucleation or growth of precipitates have occurred during aging.

The EDS (SEM) analyses performed in the extracted residues indicated the presence of Fe, Cr, W, V, Ta and Ti. Except Ti, all these elements were detected in the as-received state. The V (~5 at.%), W (~2 at.%), Ta (~2 at.%) and Ti (~0.5 at.%) contents remain practically constant in all material conditions. The most pronounced variation was in the case of Cr and Fe at 600 °C. The Cr content increased from 66.6 at.% (as-received condition) to 74.8 at.% (600 °C/5000 h). At 500 and 600 °C the Cr and Fe level variation was similar to those detected in aged material at 600 °C/5000 h, although less pronounced. Similar trend in the Cr and Fe concentrations has been observed by other authors [6,7] as a result of aging treatments at 550 and 600 °C for long times.

The X-ray diffraction patterns showed the same types of precipitates as those detected in the as-received state, e.g. $M_{23}C_6$ as predominant carbide and precipitates with the same structure as TaC.

3.1.3. Transmission electron microscopy

The Eurofer'97 in as-received condition contained $M_{23}C_6$ carbides as main precipitates (~25–210 nm size), distributed preferentially along grain and subgrain boundaries, and MX type particles rich in Ta and/or V (~8–40 nm size) located mainly inside the subgrains [8].

The aged materials showed similar characteristics by transmission electron microscopy to those found in the as-received condition. The martensite laths width values of all aged materials were similar to the as-received state (0.5 ± 0.2 μm). The only different feature was seen in the materials aged at 500 and 600 °C for 10 000 h. In these materials the occasional appearance of equiaxed grains was detected, Fig. 1, which probably indicate some recrystallization during the thermal aging treatments because neither in the as-received state nor in the other material conditions were equiaxed grains found. In the

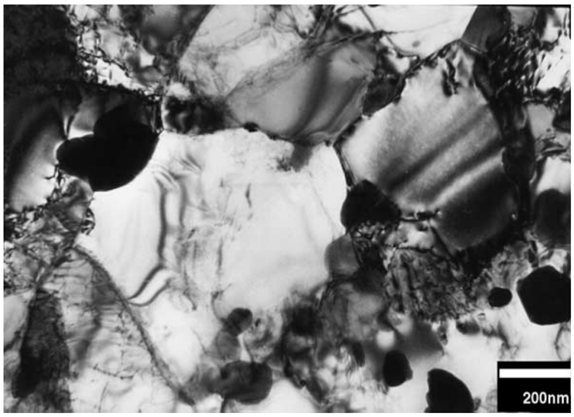

Fig. 1. TEM micrograph of equiaxed grains detected in aged material at 500 °C/10000 h.

majority of the cases, the recrystallized grains were decorated with big $M_{23}C_6$ carbides (up to 350 nm size) in their boundaries and they were free or contained only a few dislocations and precipitates inside the grains. It is well known [9] that the mobility of the lath interfaces increases as the growth and coarsening of the $M_{23}C_6$ carbides proceed, specially if these particles are principally responsible for the pinning of the lath boundaries. Consequently, such growth and/or coarsening would be expected to promote the tendency for the progressive breakdown of the martensite lath morphology during prolonged exposure at high temperature, as seems to have been the case of the Eurofer'97 aged at 500 and 600 °C for 10 000 h in this work. Partially recrystallized regions have also been observed in the F-82H mod. steel in the as-received condition as well as after thermal aging treatments at 600 °C for 5000 h and at 550 °C for 13 500 h [6,10].

3.1.4. Microchemistry at grain boundaries

The grain boundary microchemistry observed in the as received condition consisted of chromium enrichment and iron depletion as can be seen in the histograms of Fig. 2. In spite of the scatter, higher chromium concentrations are clearly seen on the intergranular areas than on the ductile ones. No any other elements were detected at the grain boundaries of the as-received Eurofer'97 steel.

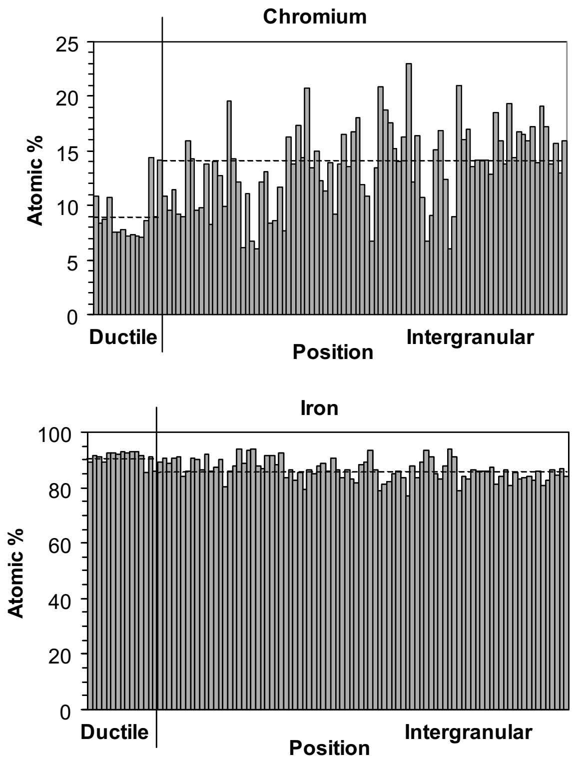

Fig. 2. Histograms of chromium and iron. Eurofer'97 as-received.

After the aging treatments at 400, 500 and 600 °C chromium enrichment and iron depletion were also detected at the grain boundaries. This chromium enrichment was more pronounced in the heat treatments performed at 500 °C for 1000 and 5000 h than in the rest of the conditions. In addition, phosphorus was also detected, but only at the grain boundaries of the materials with the thermal treatments at 500 °C.

Chromium enrichment and iron depletion have been reported in martensitic steels in the annealed and tempered condition [11–13]. This chromium enrichment was attributed to segregation in some cases [11] and to the presence of chromium carbides in other studies [12]. The literature has also reported the segregation of chromium to grain boundaries in aged ferritic/martensitic steels [14].

In this work, chromium enrichment at the grain boundaries was detected by sputtering up to depths in the range from 10 nm to more than 100 nm. On the other hand, the Eurofer'97 microstructure has shown large amounts of chromium carbide precipitation ($M_{23}C_6$) along grain boundaries with size ranges between 25 and 210 nm. Therefore, these carbides rich in chromium can be the cause of the observed chromium enrichment but it is not possible to discard the existence of some chromium segregation.

With respect to phosphorus, it was only observed after aging at 500 °C for 1000, 5000 and 10 000 h. This element was detected by sputtering only to depths less than 3 nm, indicating clearly in this case that it is segregated. Segregation of phosphorus has also been reported in aged martensitic steels [11–15]. According to Guttmann [15], martensitic steels rich in chromium are prone to intergranular embrittlement by equilibrium phosphorus segregation at temperatures between 400 and 600 °C, with phosphorus concentrations as low as 80 ppm. In the present study phosphorus has only been detected after the heat treatments at 500 °C that could be due to the low phosphorus concentration in the Eurofer'97 steel, only 50 ppm. However, in previous studies performed on the F-82H mod. steel aged at 400, 500 and 600 °C a similar behaviour was observed, i.e. phosphorus segregation to the grain boundaries only after aging at 500 °C [13].

Fig. 3 shows the distribution of phosphorus at the intergranular areas of the samples aged at 500 °C. The average values are indicated by arrows. After 1000 and 5000 h a similar phosphorus distribution was observed, but after 10 000 h the percentage of analyses with phosphorus is lower and the average concentration is also lower than in the previous cases.

According to the literature, phosphorus grain boundary segregation induced during aging occurs by an equilibrium process [16] and therefore it is unusual that

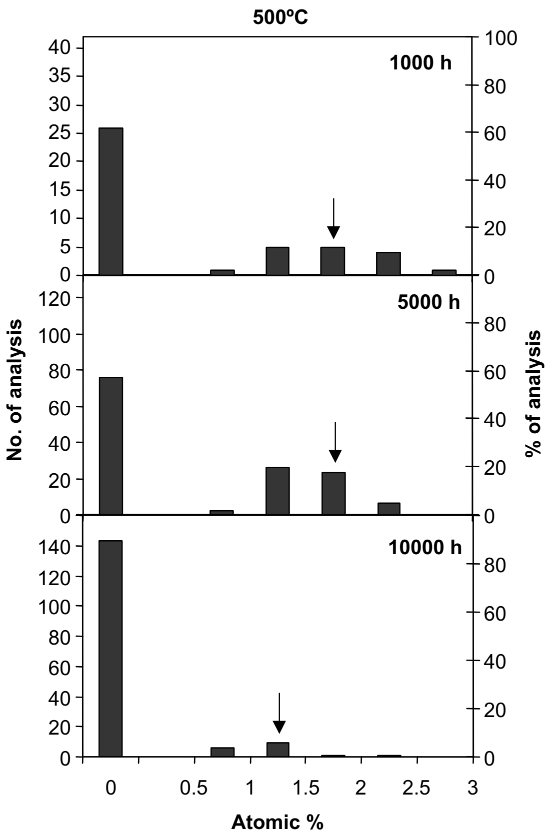

Fig. 3. Distribution of phosphorus at the intergranular areas of Eurofer'97 aged at 500 °C. Arrows indicate the average values.

after long aging treatments the amount of phosphorus decreases. However, a similar effect to the one observed in this work has been detected by Briant [17] in an austenitic steel aged at 600 and 650 °C. The author explains that large chromium additions decrease the solubility of phosphorus in γ-Fe and, therefore, enhance segregation since there is usually an inverse relationship between solubility and segregation. He also suggests that the decrease in phosphorus segregation correlates with chromium depletion. On the other hand, a decrease in phosphorus segregation has also been observed with the aging time in a martensitic steel aged at 500 °C. This decrease was produced by an increasing proportion of phosphorus incorporated in the Laves phase at the grain boundaries during aging [16].

In the present study we do not have a proven explanation for this point. A similar hypothesis to the one given by Briant could be applied. The increase in phosphorus segregation at 500°/1000 h and 500 °C/5000 h could be related to the more pronounced chromium enrichment observed at the grain boundaries after these treatments. On the other hand, the presence of recrystallized grains was observed during the aging treatment at 500 °C/10 000 h, these grains being decorated with $M_{23}C_6$ carbides bigger than the ones observed after 1000 and 5000 h. The presence of these carbides could produce a decrease of the chromium level around them, raising the solubility of phosphorus and causing desegregation of this element. With respect to the explanation offered by [16], no Laves phases have been found in this material, however it has been reported [18] that $M_{23}C_6$ carbides can dissolve considerable amounts of phosphorus and, therefore, producing a decrease in phosphorus segregation.

3.2. Mechanical properties

The results of tensile tests carried out on aged Eurofer'97 are shown in Fig. 4. Tensile characteristics in the range of temperatures from 400 to 600 °C up to 5000 h were described in Ref. [8]. As in the other material conditions, aging at 400, 500 and 600 °C for 10 000 h do not cause degradation of the tensile strength properties. These results are in accordance with the hardness measurements performed on all the aged conditions studied. The hardness level of Eurofer'97 remains quite stable after the thermal aging treatments, around 210 HV30 as in the as-received condition. The tensile and hardness results confirm the high microstructural stability observed in the Eurofer'97 steel after aging.

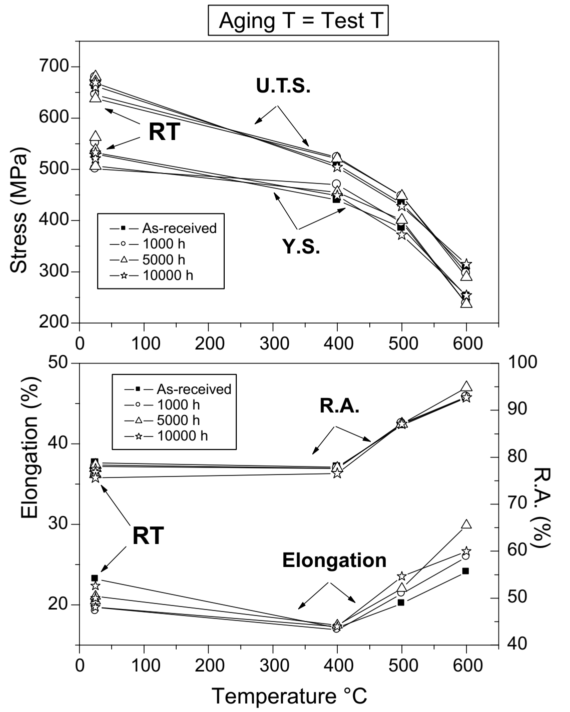

Fig. 4. Tensile tests of Eurofer'97 steel. (RT = room temperature test).

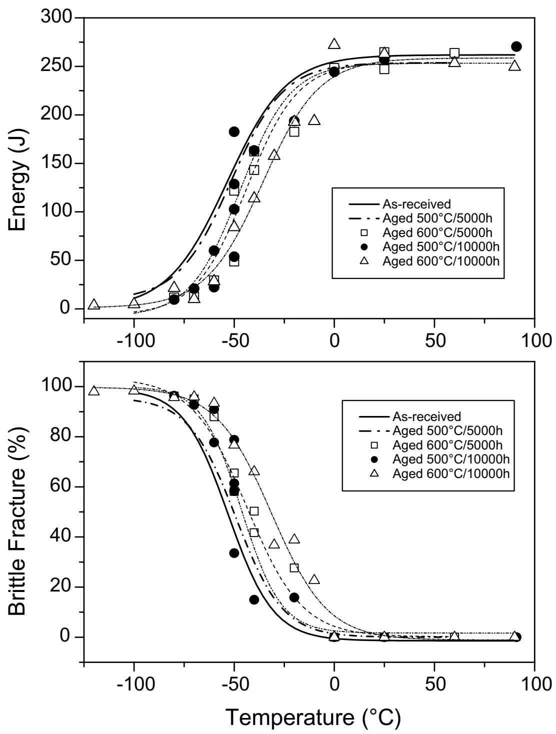

Fig. 5. Charpy tests of Eurofer'97 steel.

Charpy tests were performed on as-received material and aged materials at 500 and 600 °C for 5000 and 10 000 h (Fig. 5). Previous Charpy results on as-received and aged material at 500 °C/5000 h were reported in Ref. [8]. The Eurofer'97 steel does not show an appreciable decrease of the USE after the aging treatments investigated. However, the DBTT does increase due to the aging, this increase being most significant after aging at 600 °C/10 000 h. This material condition produces a DBTT shift of approximately 23 °C with respect to the as-received state. Taking into account the microstructural investigations, the DBTT increase could be related to the martensite transformation to sub-grains after long-term aging. However, no references have been found in the bibliography that relates these microstructural features to the impact properties.

4. Conclusions

The Eurofer'97 steel did not exhibit significant microstructural changes after the thermal aging treatments investigated in this work, from 400 to 600 °C and up to 10 000 h. The only microstructural differences was found in the materials aged at 500 and 600 °C for 10 000 h due to the occasional appearance of equiaxed grains and sub-grain structure replacing the martensite laths.

The grain boundary microchemistry observed in Eurofer'97 in the as received condition and after the aging treatments at 400, 500 and 600 °C consisted of chromium enrichment and iron depletion. In addition, phosphorus segregation was observed at the grain boundaries only in the materials aged at 500 °C.

The Eurofer'97 steel showed, for each test temperature, similar values of ultimate tensile strength and 0.2% proof stress regardless of aging condition.

No significant change in the USE was observed after the aging treatments studied. The DBTT exhibited a slight increase (~23 °C) after aging at 600 °C/ 10 000 h.

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