

Fracture Behavior of EUROFER'97 Steel After Thermal Ageing

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Abstract. Ferritic-martensitic reduced activation steel Eurofer'97 is candidate structural material for in-vessel components of proposed fusion reactors. The use of the steel is limited up to a temperature about 550 °C. On the other hand the efficiency enhancement of the fusion reactors to the level suitable for energy production is predetermined by an increase of temperature in reactor. The long term exposition of the steel at high temperatures leads to microstructural changes. The aim of the work was to investigate the influence of short and long term thermal ageing on fracture properties of Eurofer'97 steel. Short term thermal ageing of the steel was simulated by step-cooling treatment and long term thermal ageing was simulated by isothermal annealing treatment at 550 °C/5000 h. Charpy impact tests were applied to compare the fracture resistance of the sheet before and after thermal ageing. No evident changes in impact properties have been registered comparing the properties of the steel in as-received state and in state after step-cooling. Outstanding embrittlement of the thermally aged steel was observed after long term isothermal ageing.

Introduction

Ferritic-martensitic steels of (9-12)Cr-1Mo(W-Ni-V) type were developed for high temperature applications in nuclear power industry. These steels are nowadays under consideration as structural materials for perspective power sources: (i) fission reactors based on ²³⁵U a ²³²Th cycles [1], (ii) acceleration driven systems [2] and (iii) fusion reactors with magnetic plasma confining [3]. Several versions of RAFM (reduced activation ferritic martensitic) steel of (9-12)Cr-X type have been developed in Europe [4,5], Japan [6,7], USA [1] and China [8]. The most advanced version, the 9Cr-1W(V-Ta) Eurofer'97 steel, was selected as a structural material for DEMO fusion power plant prototype in-vessel and first wall components (outboard blanket) [4].

Operational embrittlement and subsequent brittle behaviour of the steels used in nuclear power industry is affected by synergy of two main influences: thermal and radiation damage. Radiation damage of the Eurofer'97 steel and elimination of its effect on mechanical properties is broadly studied as a preferred problem. There are also microstructural changes connected with operation temperatures (considered in the range 550 °C – 650 °C) such as carbidic reactions, grain coarsening and grain boundary embrittlement [9,10]. Detailed understanding of failure mechanisms of Eurofer'97 steel in as-received thermally unaffected state and state after thermal ageing is critical for its proposed future applications.

The subgrain structure of Eurofer'97 steel in the as-received state composed of martensite laths of thickness ca. 500±200 nm. Also two main populations of carbides were identified in microstructure: Cr-rich carbides of the type M₂₃C₆, predominantly located on boundaries of prior austenite grains and martensite laths, and Ta and V-rich carbides of MX type located particularly inside of martensite laths [11]. Outstanding microstructural changes of Eurofer'97 steel after thermal ageing have been described, even at the temperatures lower than considered for application [10,12] (see Fig. 1). Coarsening of martensite laths, coarsening of carbides and segregation of P to grain boundaries was observed in particular already after 1000 h thermal ageing at 500 °C and

600 °C. The segregation of P on grain boundary appeared to be connected with coarsening of carbides. Carbide coarsening caused Cr depletion of grain boundaries and allowed subsequent P segregation. The steel was also after 10000 h of thermal ageing partially recrystallized to equiaxed ferrite grains of diameter ca. 1 µm decorated by coarse (up to 350 nm) $M_{23}C_6$ carbides.

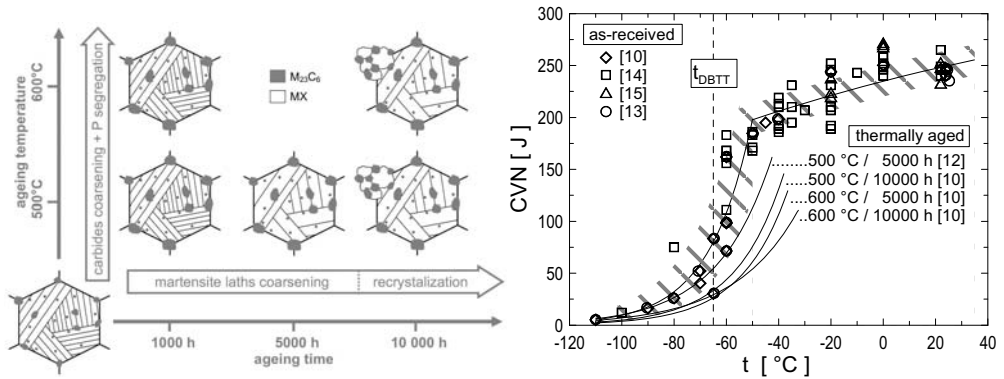


Fig. 1 Microstructural changes of Eurofer'97 steel after long term thermal ageing (left) and subsequent change in the Charpy impact energy temperature dependance (right)

The temperature dependence of impact energy for 14 mm sheet of Eurofer'97 in the as-received state including scatter band of data collected from literature [10,13,14,15] is given in Fig. 1. Data representing the influence of long term thermal ageing on impact energy of 14 mm Eurofer'97 steel published in literature [10,12] are also compiled in Fig. 1. It is evident, that thermal ageing 5000 h at 500 °C and 600 °C led to t_{DBTT} shift by ca. +10 °C and +15 °C respectively (t_{DBTT} was -65 °C for 14 mm sheet in as-received state). The long term thermal ageing at 10000 h at 500 °C and 600 °C led to t_{DBTT} shift ca. +20 °C and +25 °C respectively. The slight t_{DBTT} shift after thermal ageing at 5000 h and the evident t_{DBTT} shift after long term thermal ageing at 10000 h were explained just by partial recrystallization of martensite matrix to the ferrite grains [10,12]. The P segregation observed already after short term (1000 h) ageing was not described in literature, whereas this mechanism could lead to anomalous fracture behaviour. Grain boundary impurities enrichment leads generally to decrease of grain cohesion and consequently to intergranular fracture [16].

The aim of the work was to investigate the impact fracture behaviour and describe influence of short term and long term thermal ageing on fracture properties of Eurofer'97 steel.

2. Experimental procedure

Two sheets of different thickness (14 and 25 mm) of Eurofer'97 steel were used for experiments. The chemical composition of the sheets was verified by emission spectral analysis (Spectrumat GDS 750, Leco).

The microstructure of Eurofer'97 sheets was observed in sections perpendicular to rolling direction by means of light optical (BX 51, Olympus), scanning electron microscopy (JSM 6460, Jeol) and transmission electron microscopy (CM12, Philips). The standard metallographic procedure was used for metallographic specimens preparations. Microstructure was then chemically etched and prior austenite grain size was evaluated according to ASTM standard E112.

Short term thermal ageing (if any, supposed to be caused mainly by P segregation to grain boundary) was simulated by means of step-cooling treatment. Procedure used in this work was developed and proven for P segregation in martensitic EM-10 steel of 9Cr-1Mo(Ni) type [2]. The

applied step-cooling treatment consisted of five stages: 650 °C/1 h, 590 °C/15 h, 575 °C/24 h, 550 °C/48 h and 520 °C/72 h.

Long term thermal ageing (supposed to be caused mainly by coarsening of martensite laths, coarsening of carbides and partial recrystallization) was simulated by isothermal ageing at 550°C for 5000 h.

Fracture behaviour of Eurofer'97 steel was studied on the steel in the as-received and in the aged states by means of standard Charpy V-notch specimens tested in temperature range between -110 °C and +22 °C. The instrumented Charpy pendulum (Zwick/Roell) was used enabling to obtain load-deflection curves and determine additional fracture characteristics: yield force F_{gy} , maximum force F_m and t_{gy} general yield temperature (defined as temperature of coincidence of general yield force F_{gy} and fracture force F_m on their temperature dependence).

Fracture surfaces were studied by means of light optical (BX 51, Olympus) and scanning electron microscopy (JSM 6460, Jeol) enabling to recognize fracture initiation site and to identify fracture propagation mechanism.

3. Results and discussion

The chemical composition of the 14 mm and 25 mm sheets used corresponded to nominal chemical composition of Eurofer'97 steel except the double content of molybdenum and alumina (see Tab. 1). The content of phosphorus was lower than the Eurofer'97 steel specification requires. The content of nickel exceeded three times the required level in the case of examined materials. The question is how these differences in the chemical composition can affect microstructural features and fracture behaviour of Eurofer'97 steel.

Table 1: Chemical composition of Eurofer'97 steel sheets used in wt.%

element	C	Cr	W	V	Ta	Mn	Si	Ni	Mo	Al	P
nominal composition	0.09 0.12	8.5 9.5	1.00 1.20	0.15 0.25	0.10 0.14	0.20 0.60	0.05	0.01	0.005	0.01	max. 0.005
14 mm sheet	0.11	8.7	1.07	0.23	0.12	0.55	0.03	0.03	0.01	0.02	0.001
25 mm sheet	0.11	8.8	1.09	0.23	0.14	0.56	0.03	0.03	0.01	0.02	0.003

The thermal treatment of as-received sheets consisted of austenitization (980 °C/21.6 min/air) and subsequent annealing (760 °C/90 min/air). The microstructure of 14 mm and 25 mm Eurofer'97 sheets in the as-received state was then fully martensitic (see Fig. 2) with equiaxed prior austenitic grains of size $8.3 \pm 0.5 \mu\text{m}$ and $8.3 \pm 1.0 \mu\text{m}$ respectively. These values were comparable to the results published by Fernandez et al. [11]: $8.8 \pm 2.2 \mu\text{m}$ for the 14 mm sheet and $8.7 \pm 0.7 \mu\text{m}$ for 25 mm sheet. The prior austenite grain boundaries were decorated by carbides that corresponded mainly to Cr-rich $M_{23}C_6$ carbides of size up to 200 nm. This was in accordance with results obtained by Fernandez [11] which denotes $M_{23}C_6$ carbides sizes distribution frequency in Eurofer'97 from 25 nm to 210 nm with mean value of 75 nm.

Considering the analytical method applied for microstructure evaluation it was impossible to verify the presence of P on grain boundaries after step-cooling treatment, especially in the case of low phosphorus content in the Eurofer'97 steel. Thus, no change in the microstructure of Eurofer'97 was observed, between the as-received and the step-cooled state. Also no outstanding changes in the microstructure after isothermal annealing at 550 °C/5000 h were observed. The isothermal ageing used caused mainly martensite laths coarsening: the average thickness of martensite laths were $500 \pm 200 \text{ nm}$ for the steel in the as-received state and $600 \pm 200 \text{ nm}$ for the steel after isothermal

ageing at 500 °C/5000 h. Also carbide coarsening was observed as a consequence of long isothermal ageing [12].

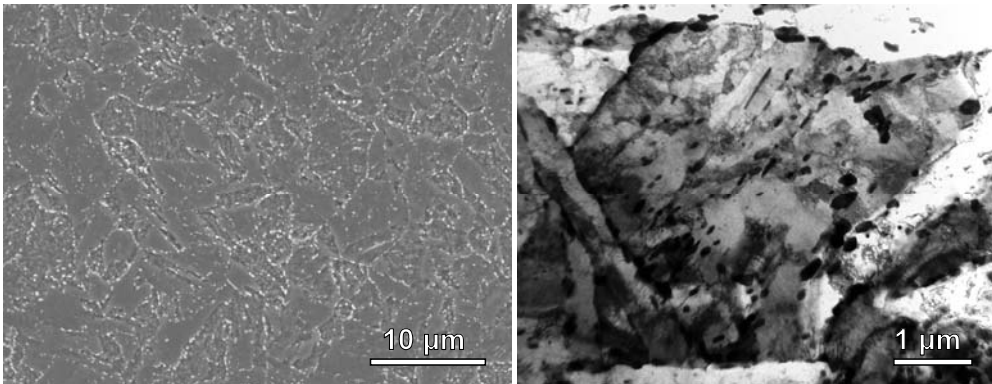


Fig. 2. Microstructure of Eurofer'97 steel in as-received state (SEM – left, TEM – right)

The radiation damage and its effect on mechanical properties of Eurofer'97 steel was studied at literature broadly [17,18]. For evaluation of the radiation damage influence on fracture properties the Charpy V-notch test is widely used as a standard method. This was the main reason why the Charpy test is also used for evaluation of effect of thermal ageing on mechanical properties. Nevertheless the Charpy test application only without any additional method of fracture behaviour characterization is questionable [13], among others because of in-plane and out-of-plane crack-tip constraint effects [19,20].

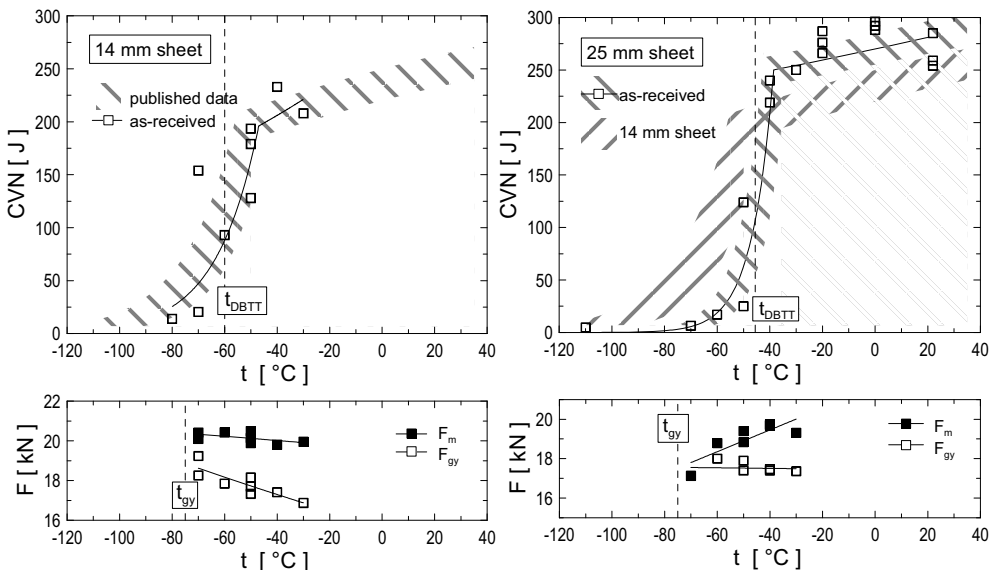


Fig. 3 Charpy impact energy temperature diagram of 14 mm sheet (left) and 25 mm sheet (right) of Eurofer'97 in as-received state (upper – temp. dependance of impact energy, lower – temp. dependance of F_{gy} and F_m)

The measured temperature dependence of absorbed energy for 14 mm sheet compared with values collected from literature is given in left part of Fig. 3. It is evident that the impact energy of 14 mm Eurofer'97 steel was comparable with published results. The t_{DBTT} temperature determined as a halfway between the upper and lower shelf impact energy, was close to the literature data (see Fig. 1) and was about $-60\text{ }^{\circ}\text{C}$. Data obtained from instrumented Charpy impact tester made possible to determine general yield temperature t_{gy} of 14 mm sheet. The t_{gy} temperature determined from the temperature dependence of general yield force F_{gy} and maximum force F_m , was about $-75\text{ }^{\circ}\text{C}$. The cleavage mechanism of crack initiation and propagation in Eurofer'97 steel in the as-received state under the conditions of brittle fracture (near t_{gy} temperature) was identified (see Fig. 5a) by means of microscopic examinations of fracture surfaces.

The measured thermal dependence of impact energy for 25 mm sheet in the as-received state compared with values for 14 mm sheet is given in right part of Fig. 3. A completely different fracture behaviour of 25 mm sheet compared with 14 mm one was observed. The transition temperature t_{DBTT} of 25 mm sheet was shifted by ca. $+20\text{ }^{\circ}\text{C}$ to the temperature $-45\text{ }^{\circ}\text{C}$ and upper shelf energy level of 25 mm sheet was higher by about 50 J. In the as-received state the temperature curve obtained for 25 mm sheet embodied very sharp transition and larger scatter than transition temperature curve for 14 mm sheet. The F_{gy} and F_m forces of the 25 mm sheet reached lower values than in the case of 14 mm sheet. It is evident from the temperature dependence of F_{gy} and F_m , that no change of t_{gy} temperature was observed in the case of 25 mm sheet comparing to 14 mm sheet. Microfractographic examinations of specimens broken near t_{gy} temperature revealed cleavage mechanism of brittle fracture initiation and propagation (see Fig. 5b). No reasons for observed differences in temperature dependence of impact energy were observed in the microstructure and chemical composition, despite of using two different heats of Eurofer'97 steel. The differences in chemical composition of both heats used were of the order of hundredths of wt.% what is in the value as limit of analytical method used (see Tab. 1). The reason for Charpy impact energy variation could be find in different deformation history of two sheets of different thickness used.

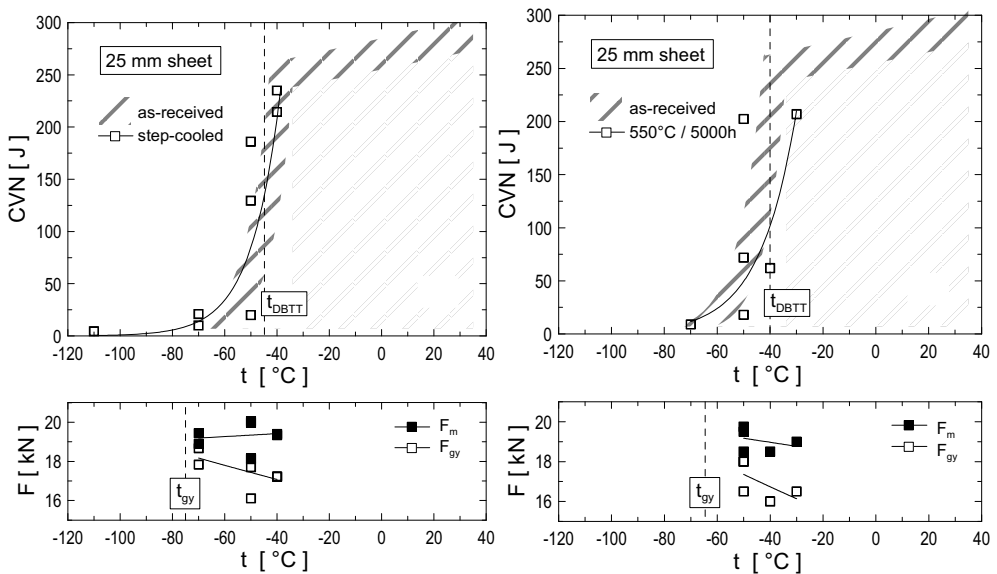


Fig. 4 Charpy impact energy temperature diagram of 25 mm sheet of Eurofer'97 after simulated short term (left) and long term (right) thermal ageing (upper – temp. dependence of impact energy, lower – temp. dependence of F_{gy} and F_m)

No difference between temperature dependance of impact energy of 25 mm sheet in the as-received state and in state after step-cooling was observed (see Fig. 4). Step-cooled 25 mm sheet showed no evidences of thermal embrittlement. Impact energy of the step-cooled 25 mm sheet lied in the scatter band of the as-received 25 mm sheet. Values of t_{DBTT} temperature and t_{gy} were similar as in the case of 25 mm sheet in the as-received state and were $-45\text{ }^{\circ}\text{C}$ and $-75\text{ }^{\circ}\text{C}$ respectively. Fractographic examinations revealed no presence of intergranular fracture (e.g. as a consequence of grain boundary weakening by phosphorus segregation) in the case of step-cooled steel. Thermally aged Eurofer '97 steel fractured near t_{gy} temperature by cleavage mechanism and the cleavage being triggered by secondary phase was observed (see Fig. 4c).

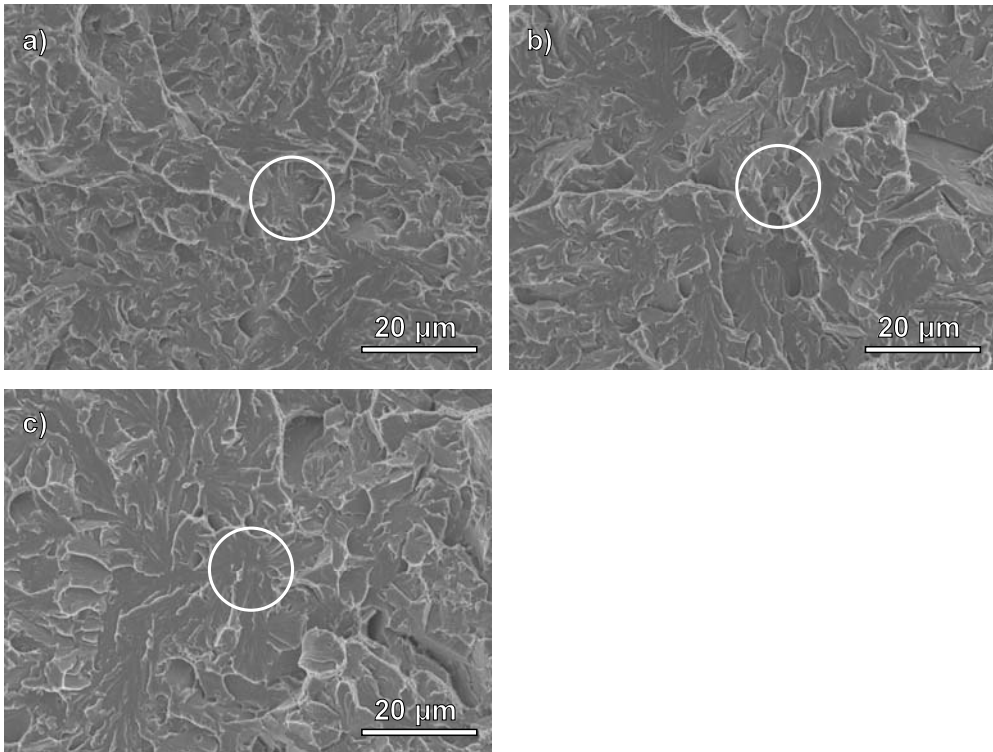


Fig. 5. Fracture surface of Eurofer '97 steel in the initiation site location (encircled)
(a – 14 mm sheet in as-received state, b – 25 mm sheet in as-received state,
c – 25 mm sheet in step-cooled state)

Evident shift of temperature dependance of impact energy of 25 mm sheet after isothermal ageing at $550\text{ }^{\circ}\text{C}/5000\text{ h}$ was observed in comparison with the steel in as-received state (see Fig. 4). Values of t_{DBTT} temperature and t_{gy} of isothermally aged 25 mm Eurofer '97 steel were $-40\text{ }^{\circ}\text{C}$ and $-65\text{ }^{\circ}\text{C}$ respectively and were shifted by about $+5\text{ }^{\circ}\text{C}$ and $+10\text{ }^{\circ}\text{C}$ respectively.

Long term thermal ageing at $500\text{ }^{\circ}\text{C}/10000\text{ h}$ and $600\text{ }^{\circ}\text{C}/10000\text{ h}$ and subsequent embrittlement of the Eurofer '97 steel described in the literature [10] led to t_{DBTT} shift by ca. $+20\text{ }^{\circ}\text{C}$ and $+25\text{ }^{\circ}\text{C}$ respectively. The observed embrittlement was in the literature associated with the microstructural changes, especially to the partial recrystallization of martensite microstructure to the equiaxed ferrite grains. Limited effort was given however to the carbide coarsening. This change of carbide

size values [12] can be reflected by change in fracture behaviour, namely the cleavage triggering mechanism of the Eurofer'97 steel. The growth of carbides of $M_{23}C_6$ type from 40-260 nm to 40-300 nm was observed after thermal ageing at 500 °C/5000 h and 600 °C/1000 h respectively.

In the work of Fernandez [10] the segregation of phosphorus on to grain boundaries was noted after ageing at 500 °C/5000 h a 500 °C/10000 h, it means at the lower limit of the considered exploitation range for the steel. With respect to the low phosphorus content (up to 0.005 wt.%) a risk of grain boundary weakening by phosphorus segregation is very low while the carbide coarsening could led to real embrittlement of the Eurofer'97 steel.

4. Conclusions

The influence of thermal ageing on fracture properties of 14 mm and 25 mm sheets of Eurofer'97 steel was investigated. The thermal ageing of the Eurofer'97 steel was simulated by step-cooling treatment and long term isothermal annealing treatment. Charpy impact tests were performed before and after thermal ageing and impact energy, ductile-to-brittle transition temperature t_{DBTT} and general yield temperature t_{gy} were evaluated. Impact fracture behaviour of 14 mm sheet corresponded to the literature data. Transition temperatures t_{gy} and t_{DBTT} of 14 mm sheet were -75 °C and -60 °C respectively. A completely different impact fracture behaviour of 25 mm sheet in comparison with 14 mm one was observed. Shift of t_{DBTT} by about +20 °C to the value ca. -45 °C was observed. Transition temperature t_{gy} achieved value about -75 °C. No difference between temperature dependence of impact energy of 25 mm sheet in as-received state and in state after step-cooling was observed. It was found, that under the conditions of brittle fracture (near general yield temperature t_{gy}) crack initiated and propagated by cleavage mechanism in the as-received and step-cooled Eurofer'97 steel with no evidences for grain boundaries weakening due to phosphorus segregation. The isothermally aged specimens embodied t_{DBTT} and t_{gy} shift by about +5 °C and +10 °C respectively in comparison with 25 mm sheet in the as-received state. This behaviour could be associated to carbide coarsening observed. A risk of grain boundary weakening by phosphorus segregation is very low while the carbide coarsening could led to outstanding embrittlement of the Eurofer'97 steel.

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