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Grain size reduction strategies on Eurofer

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ABSTRACT

One of the options currently taken into account for the realization of the first DEMO reactor is the “water-cooled blanket”. This option implies a minimum irradiation temperature for the blanket material in the range of 280–350 °C. In addition to the DBTT (Ductile to Brittle Transition Temperature) shift due to the DPA (displacement per atom) damage under irradiation, also the issue of the increased embrittlement due to He production must be taken into account. This issue appears even more detrimental and less manageable because the DBBT shift due to the Helium production does not saturate with the dose, as it results from previous works reported in literature. The experimental results and the difference in behaviour between ODS (Oxide Dispersion Strengthened Steels) RAFM (Reduced Activation Ferritic Martensitic) and other FM (Ferritic Martensitic) alloys (EM10, P91) showed that it is possible to improve the resistance to He embrittlement by both intra-granular precipitation of Y-Ti oxides and by decreasing the grain size at the same time. Nevertheless, anyway, the multiplication of the grain boundaries increases the dilution of He on grain surface, delaying the formation of He bubbles on grain boundaries and, therefore, the susceptibility to the He embrittlement. Several grain size reduction strategies have then been investigated on EUROFER both at the austenitization stage, on the PAGS (Prior Austenite Grain Size), and at the tempering stage, on the tempered martensite. The microstructural observations have been carried out by means of SEM (Scanning Electron Microscopy). Also the effect of grain size reduction on the toughness of the material will be taken into account; The DBTTs resulting from impact tests on KLST specimens will be shown. The outcomes of the microstructural observations, as well as the preliminary mechanical characterization (impact tests) will be discussed in this paper.

1. Introduction

One possible scenario for the realization of the first DEMO reactor is the adoption of the “water-cooling”. This option implies a minimum irradiation temperature for the blanket material in the range of 280–350 °C. Therefore, in light of the under irradiation behaviour of EUROFER the target of the hereby reported activities is the development of much tougher alloys, suitable to tolerate such a low irradiation temperature. In addition to the DBTT (Ductile to Brittle Transition Temperature) shift due to the DPA (displacement per atom) damage under irradiation, also the issue of the increased embrittlement due to He production must be taken into account. This issue appears even more detrimental and less manageable because the DBBT shift due to the Helium production does not saturate with the dose, as it results from previous works reported in literature [1]. The multiplication of the grain boundaries increases the dilution of He on grain surface, delaying the formation of He bubbles on grain boundaries and, therefore, the susceptibility to the He embrittlement.

Several grain size reduction strategies have then been investigated on EUROFER both at the austenitization stage, on the PAGS (Prior Austenite Grain Size), and at the tempering stage, on the tempered martensite. As demonstrated by some experimental data [2], Eurofer exhibits different irradiation behaviour as a function of normalizing temperature. In particular, according to Gaganidze et al. [2], Eurofer normalized at 980 °C seems to undergo a markedly higher DBTT shift under irradiation with respect to the same material normalized at 1050 °C. This behaviour seems to be confirmed also by the irradiation of a 9Cr2WVTa [3] in FFTR (Fast Fuel Test Reactor), normalized at 1050 °C. The better behaviour after irradiation seems to be obtained with a higher normalizing temperature. This could be related to better solutioning of primary precipitation. On the other hand, according to several literature sources [4–6], thermal treatments based on multiple normalizations seem successful in achieving PAGS reduction. We set up an experimental campaign aimed at achieving meaningful PAGS

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Table 1
Test matrix of the asymmetric rolling experiments.

Test number	Pre-heating (temperature/time)	Hot working mode / section reduction ratio	Normalization	Normalization
YC25	1150 °C / 25 min	Conventional / 25	None	None
YC40	1150 °C / 25 min	Conventional / 40	None	None
YA25	1150 °C / 25 min	Asymmetric / 25	None	None
YA40	1150 °C / 25 min	Asymmetric / 40	None	None
WC25	1150 °C / 25 min	Conventional / 25	1020 °C × 30 min	None
WC40	1150 °C / 25 min	Conventional / 40	1020 °C × 30 min	None
WA25	1150 °C / 25 min	Asymmetric / 25	1020 °C × 30 min	None
WA40	1150 °C / 25 min	Asymmetric / 40	1020 °C × 30 min	None
ZC25	1150 °C / 25 min	Conventional / 25	1020 °C × 30 min	1020 °C × 30 min
ZC40	1150 °C / 25 min	Conventional / 40	1020 °C × 30 min	1020 °C × 30 min
ZA25	1150 °C / 25 min	Asymmetric / 25	1020 °C × 30 min	1020 °C × 30 min
ZA40	1150 °C / 25 min	Asymmetric / 40	1020 °C × 30 min	1020 °C × 30 min

reduction by multiplying the normalization stages and, at the same time, keeping normalization temperature higher than 980 °C. Following this strategy lower DBTT shift under irradiation is expected.

Secondly thermo-mechanical treatments using hot asymmetric rolling were taken into account [7,8]. Asymmetric rolling introduces biaxial deformations that are more effective for nucleation of new grains than conventional rolling. In addition asymmetric rolling introduces a shear component through the thickness that could help to break the textural distribution derived by the refractory grains [7,8].

Eventually the possibility to the tempered Martensite has been considered. Some works in literature are focused on the achievement of ultra-fine ferritic grains even by cold-working Martensite [9]. In order to avoid too high loads on the rolling plant, by cold working Martensite, we just focused on a particular TMT (Thermo-Mechanical Treatment) consisting in a sequence of tempering-cold working-tempering [10]. The aim of this TMT is to induce recrystallization of the laths substructure and obtain an equiaxed nano-grain structure that should be more irradiation resistant, increasing the recombination sites of point defects on nano-grains boundaries. The cold-working after tempering has a twofold purpose. The first is to destroy the crystallographic relationships between martensitic lathes generated during quenching and the second is to have a sufficient dislocation density to induce secondary recrystallization at low temperature. The second is a generally known phenomenon that relates the dislocation density, time and temperature to the grain size dimension.

2. Experimental

2.1. Multiple normalizing treatments on EUROFER 97/2

Specimens of about 2 × 2 × 2 cm of 25 mm plate of Heat 993391 (Eurofer 97/2; 9% Cr, 1% W, 0.11% C, 0.4% Mn, 0.2% V, 0.07% Ta, 0.03% N) were normalized for 30 min up to three times at the following temperatures: 1000 °C, 1010 °C, 1020 °C, 1030 °C and 1040 °C. To identify the Prior Austenite Grains, the samples were heat treated at 580 °C × 1 h to highlight the prior austenite grain and chemically etched. The prior austenitic grains were manually encircled on a printed photograph and measured by the intercept method. After that the grain size distributions have been obtained by means of the ImageJ software [12].

After the selection of the thermal treatment, a part of the 25 mm plate of Eurofer 97/2 supplied by Eurofusion was thermally treated and tested by means of impact tests on both ISO-V and KLST. KLST specimens have been extracted in L-T and T-L directions respect to the rolled plate. KLST specimens have been tested with a 25 Joule mini pendulum.

2.2. Asymmetric rolling

Starting from the EUROFER 97/2 rolled plate supplied by Eurofusion, the effect of rolling mode (conventional or asymmetric) and section reduction ratio (25 or 40%) is analyzed. The plate was hot rolled on the CSM (Centro Sviluppo Materiali) pilot scale; the following test matrix (Table 1) has been carried out, aimed at comparing the two hot working modes (conventional and asymmetric) in terms of PAGS (Prior Austenite Grain Size) refinement with the same process parameters (heating temperature, thickness reductions, final thermal treatment). The normalization stages are always followed by air cooling.

The samples have then been treated at 580 °C and etched with Oxalic acid (10 g Oxalic acid, $C_2H_2O_4$, in 100 ml H_2O) in order to detect the PAGS. The resulting PAGS are reported in the next paragraph.

2.3. Recrystallization studies

The aim of these studies was to induce low temperature recrystallization on tempered martensite using cold working. The following test matrix (Table 2) has been carried out, aimed at selecting the best combination of process parameters in terms of highest amount of achieved recrystallized micro grains. Microstructural analysis have then been performed in order to select the most promising condition among the ones tested.

In order to perform microstructural observations the samples have been treated up to the last stage of electrolytic polishing aimed at maximizing crystallographic contrast. The microstructure has then been highlighted through crystallographic contrast by back scattered electrons. The observations, reported in the next chapter, have been carried out by means of a FEG-SEM (Field Emission Gun – Scanning Electron Microscope) "Leo 1525 (Zeiss)" and a Solid State Electron Backscattered Detector.

The Vickers micro-hardness has been measured with a 10 kgf load (HV10). The thickness of the final tempered plate on which the hardness measurements have been carried out is 4.9 mm.

Table 2
Test matrix of the recrystallization experiments.

Test Number	Normalization	Normalization	Tempering	Cold Working mode (50% section reduction ratio)	Tempering
1	1020 × 30'	1020 × 30'	760 °C × 1 h	Asymmetric	720 °C × 2 h
2	1020 × 30'	1020 × 30'	760 °C × 1 h	Asymmetric	760 °C × 2 h
3	1020 × 30'	1020 × 30'	760 °C × 1 h	Conventional	720 °C × 2 h
4	1020 × 30′	1020 × 30'	760 °C × 1 h	Conventional	760 °C × 2 h

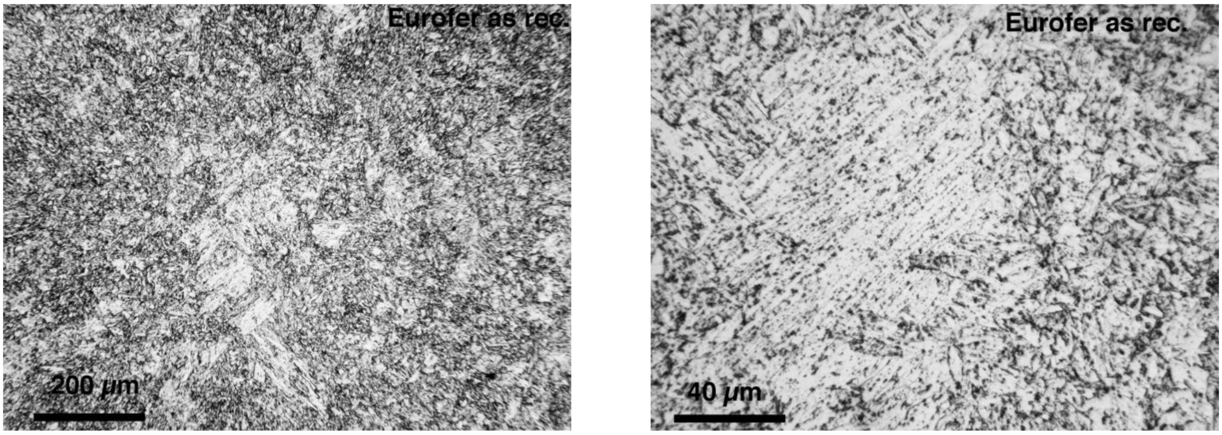


Fig. 1. Microstructure of As received Eurofer 97/2.

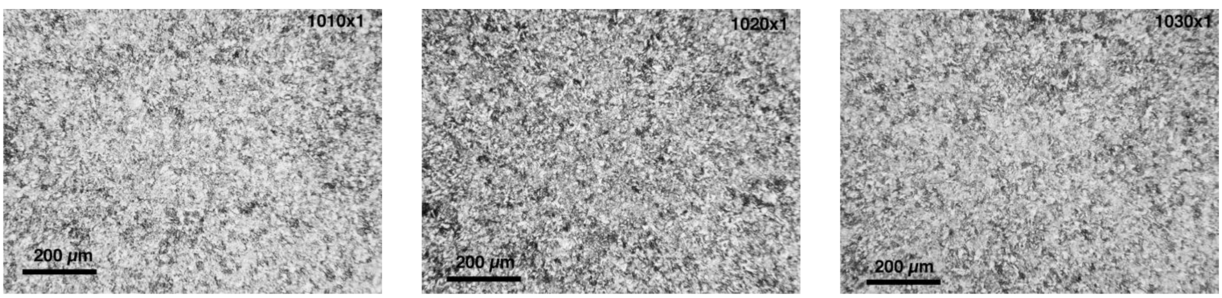


Fig. 2. Microstructure of Eurofer 97/2 after one normalizing treatment.

After the selection of the definitive thermal treatment, two portions of the 25 mm plate of Eurofer 97/2 supplied by Eurofusion were thermally treated; one portion with the conventional cold working (Double normalization 1020 °C × 30 min, Tempering 760 °C × 1 h, conventional cold working, Tempering 760 °C × 1 h); the other portion with the asymmetric cold working (Double normalization 1020 °C × 30 min, Tempering 760 °C × 1 h, asymmetric cold working, Tempering 760 °C × 1 h). The two plates have then been tested by means of impact tests on KLST specimens. It hasn't been possible to perform impact tests on ISO-V specimens (10 × 10 × 55 mm) due to the narrow thicknesses of the cold worked plates. KLST specimens have been extracted in both L-T and T-L directions in the conventionally rolled plate. Due to the bended shape of the asymmetric rolled plate it has just been possible to extract KLST specimens in T-L direction. KLST specimens were tested with a 25 J mini pendulum (test procedure according to DIN 50115).

3. Results

3.1. Multiple normalizing treatments on EUROFER 97/2

The plate of the as received Eurofer 97/2 (Heat 993391) on which the following experimental activities have been carried out was initially characterized by a inhomogenous microstructure with several exploded grains (Fig. 1). This should be likely due to a too much high heating temperature or time at the beginning of hot rolling stage and/or to some chemical micro-inhomogeneities.

Therefore, in order to re-homogeneize this original non-homogeneous micro-structure, the plate has undergone several normalization stages. The microstructural inhomogeneities resulted drastically reduced after the first normalizing treatment (Fig. 2).

The double normalization treatment appears successful in achieving a slight grain refinement (about 25%) at each tested temperature; some examples of the obtained microstructure are reported in the following figure (Fig. 3).

The grain distribution exhibits, as usual, a log-normal shape (Figs. 4 and 5). The obtained results are reported in the following Table 3.

It should be noted that the profit in terms of PAGS refinement between the first and second normalizing treatment is not so pronounced as in other RAFM steels [5]. A beneficial effect is however noticeable in terms of reduction of the grain size mean value and of the standard deviation. This implies a more homogeneous microstructure.

The results show that the beneficial effect of a multi-normalizing treatment is restricted to a number of 2. The mean grain size increases or remains stable with the third normalizing treatment. Therefore, we chose as reference treatment the following: 1020 °C × 0.5 h + a.c. + 1020 °C × 0.5 h + 760 °C × 1.5 h. The 1020 °C normalization temperature has eventually been determined as an average between the one commonly adopted for Eurofer (980 °C) and the 1040 °C used in [2,3] with its relative expected beneficial effects under irradiation.

We show in the following figure the results the results of the impact tests; ISO-V (Fig. 6) and KLST (Fig. 7 and Table 4).

By comparison, the double normalizing treatment increases the Upper shelf Energy of more than 7%, shifts the DBTT of about 6 °C toward lower temperature and the Tanh (Hyperbolic tangent) curve exhibits a smoother behaviour.

3.2. Asymmetric rolling

As it results from the next plot (Fig. 8), a marked positive effect in terms of PAGS refinement due to the hot working is detected by varying thickness reduction ratio between 25 and 40%. The grain size reduction due to this effect varies from 30% for the "as hot rolled" plate to 40% applying one austenitization stage and at last becomes negligible with two normalization stages.

Considering the thermal treatment applied on the hot rolled plate,

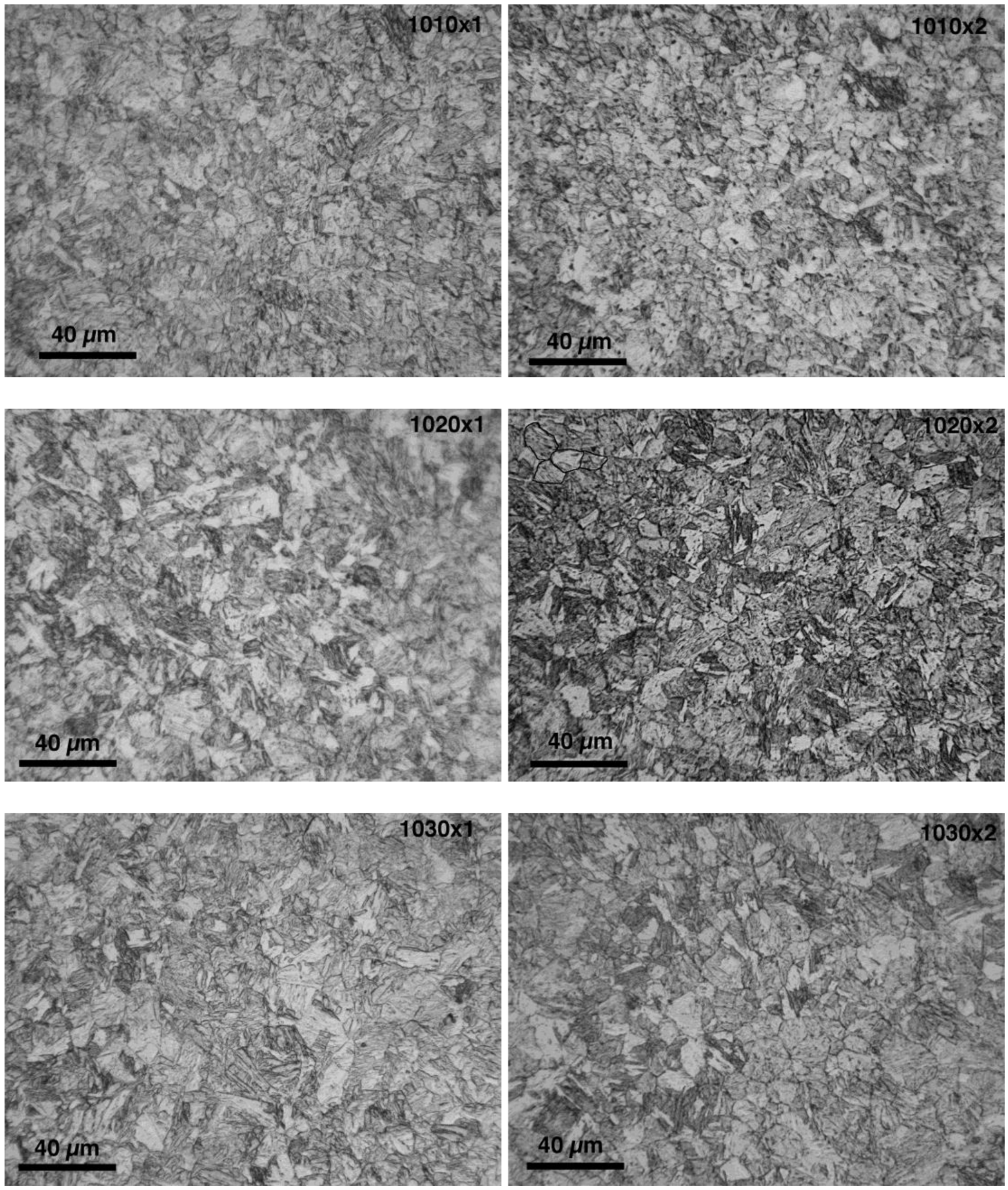
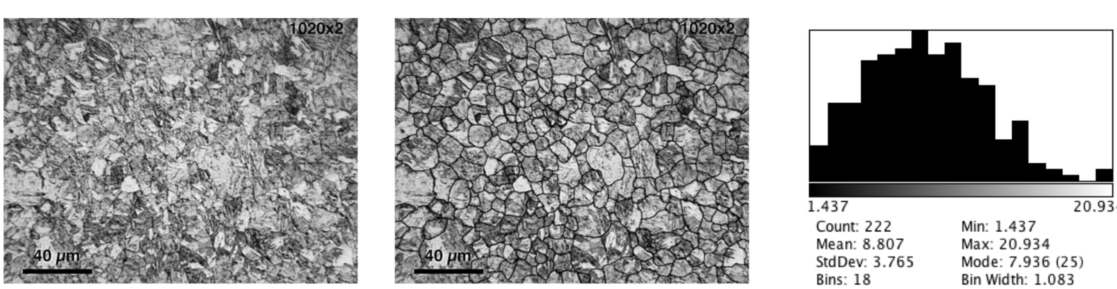


Fig. 3. Microstructure of Eurofer normalized once and twice at 1010 °C, 1020 °C and 1030 °C.



(a) (b) (c)

Fig. 4. Eurofer 1020 × 30' + a.c. + 1020 × 30' + a.c. (a) original micrograph;(b) same micrograph with encircled PAGs;(c) diameter distribution calculated as $d = (4 \times \text{Area}/\pi)^{1/2}$.

after a single normalization, the asymmetric hot rolling results markedly successful in decreasing the prior austenite grain size with respect to conventional rolling. The grain size reduction due to the effect of the asymmetric rolling, infact, varies from 6% for the "as hot rolled" condition to even 25% applying one normalization stage. Nevertheless, after two normalization cycles, the difference appears no longer meaningful or even detrimental. Then we can state that the asymmetric rolling actually takes to a marked grain refinement on the hot rolled

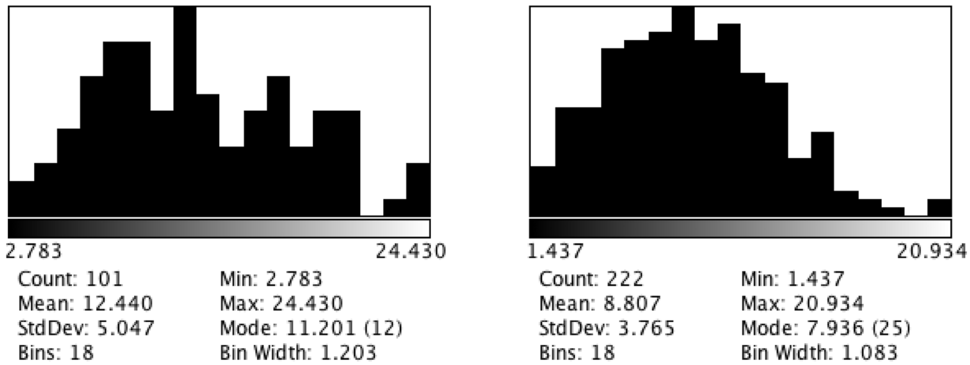


Fig. 5. Grain diameter distribution for (a) one normalizing treatment;(b) two normalizing treatment at 1020 °C × 30'.

Table 3
Statistic results of the multiple austenitization studies.

Normalizing temperature (°C)	1th normalization			2nd normalization			3rd normalization		
	Mean G.S. (µm)	S.D (µm)	Mode (µm)	Mean G.S. (µm)	S.D (µm)	Mode (µm)	Mean G.S. (µm)	S.D (µm)	Mode (µm)
1010	10.1	4.1	7.2	8.8	4.1	5.9	7.6	3.6	4.3
1020	12.4	5.0	11.2	8.8	3.8	7.9	10.6	4.1	8.1
1030	11.0	4.9	6.0	10.0	3.9	8.1	11.6	5.0	9.8

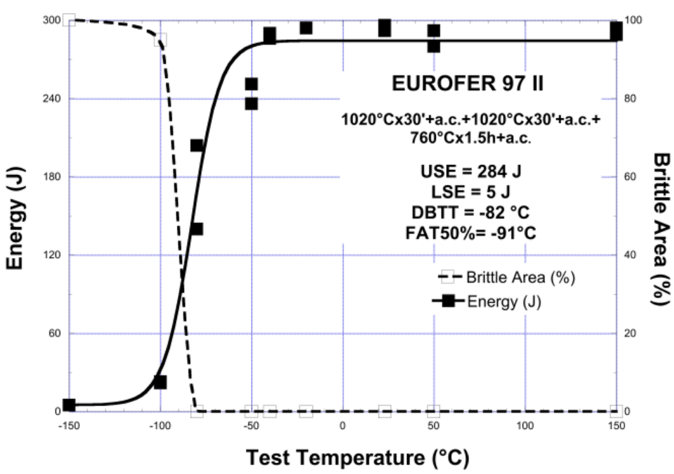


Fig. 6. Charpy Iso V results.

plate but this effect becomes negligible once the material undergoes a quality treatment with multiple austenitization stages.

3.3. Recrystallization studies

Some of the FEG-SEM microstructural observations are reported in the next figures (Figs. 9 and 10);

From all the observations we deduced what follows;

- Re-tempering after cold rolling, at least with high thickness reduction ratio, is effective to induce recrystallization at low temperature.
- The difference between Symmetric and Asymmetric Rolling is not so relevant.
- The microstructure is a mixture of very small ferritic grains (in the order or less than 1 µm) and too big ferritic ones.
- The lower the re-tempering temperature, the higher the microstructural homogeneity (fine-grains).

The hardness values, measured at the center of the thickness, range between 161 and 176 HV10. These values result markedly lower compared to the one of as received Eurofer 97/2, in the range of 220 HV [11]. This must be considered as an evidence of the achieved recrystallization. Of course a hardness value in this range is too low for the final product, but this campaign must just be considered as a screening aimed at determining the best TMT in order to obtain a fully nanostructured microstructure. In principle it will always be possible, once the definitive TMT has been determined and applied, to cold work the plate again in a range of 10–20% (section reduction ratio) in order to restore acceptable mechanical properties.

The results from the impact tests are reported in the next plots (Figs. 11 and 12) and summarized in Table 5.

Observing these results we believe that, considering the inhomogeneity of microstructure, the outcomes are promising; the DBTT is very low even if the matrix is not completely nanostructured. We suppose that the spread of the energy values in the transition region is due to the inhomogeneity of the microstructure (presence of too big ferritic grains). It's reasonable to think that, once the completely nanostructured microstructure is achieved, the DBTT would result further decreased. The comparison between Symmetric and Asymmetric rolling does not show substantial differences.

4. Conclusions

Several combinations of thermal treatments were conducted on Eurofer 97/2 in order to identify the best solution in order to refine as much as possible the Grain Size.

Multiple normalizations at different temperatures have been carried out on Eurofer 97/2 alloy aimed at identifying the best profit in terms of PAGS reduction. The obtained results indicate that the chosen thermal treatment, consisting in a double normalizing at 1020 °C and tempering, reduces the Grain Size of approximately 25% and consequently increases the toughness of Eurofer 97/2 by shifting the DBTT of about −7 °C towards the lowest temperatures (KLST samples). The selected thermal treatment fulfils two targets:

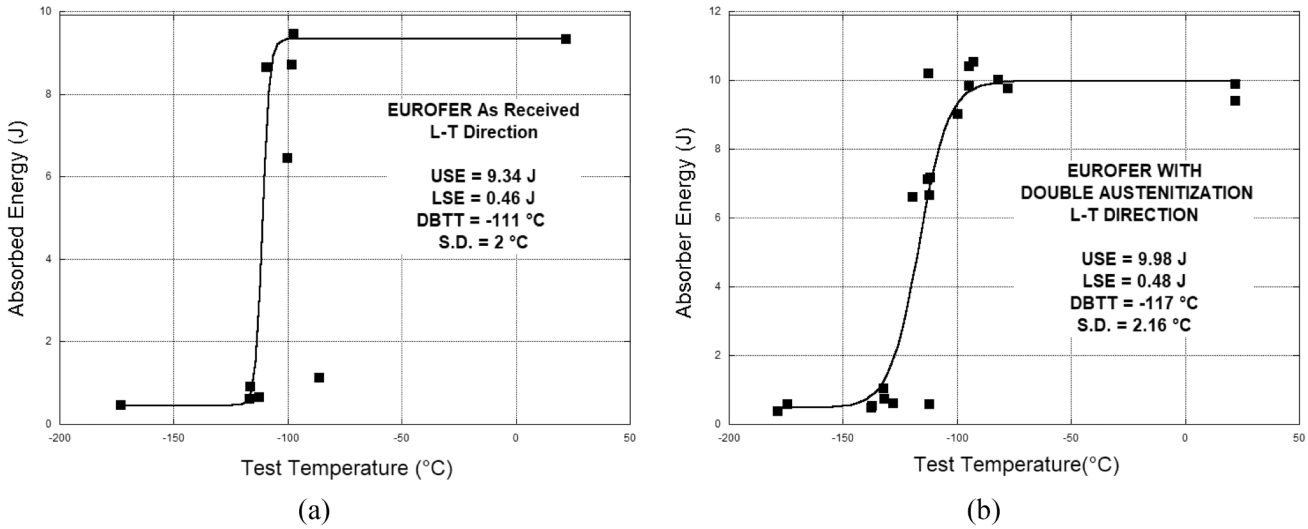


Fig. 7. KLST test results on Eurofer 97 II Heat 993391 (a) in the as received conditions and (b) after double normalization at 1020 °C × 0.5 h and tempering at 760 °C × 1.5 h.

Table 4
Mean value and Standard Deviation of the results of the DBTT on KLST specimens.

Status of Eurofer 97/2	Mean value of the DBTT	Standard Deviation
As received	−111 °C	2 °C
Double Austenitization 1020 °C	−117 °C	2.16 °C

- lowering the DBTT (even though not so much);
- increasing the normalizing temperature in order to have a final thermal treatment as much similar as possible to Eurofer WB ([2], expected improved embrittlement resistance under low temperature neutron irradiation).

The outcomes of the campaign on asymmetric hot rolling demonstrate that this treatment actually produces an effect on the reduction of the PAGS. Nevertheless this effect becomes less meaningful as long as further austenitization stages are added. These experiments show how it is possible, during the hot working stage, to act on the rolling mode (asymmetric instead of conventional) and on the section reduction ratio (the higher the c.w. ratio, the smaller the PAGS) in order to achieve marked grain refinement but this effect becomes negligible once the material undergoes a quality treatment with multiple austenitization stages.

After the tempering-cold working-tempering treatment the obtained material results effectively recrystallized but, due to high re-tempering temperature, the microstructure is inhomogeneous, with large ferritic grains and nano-structured ferritic zones. For a 50% c.w. (cold working) ratio, during re-tempering treatment, the homogeneity of the microstructure increases with the decreasing temperature. Despite the firsts attempts show an inhomogeneous microstructure consisting of very fine ferritic grains accompanied by too big ones, the impact properties are encouraging; impact tests on KLST performed on Eurofer 97/2 show an

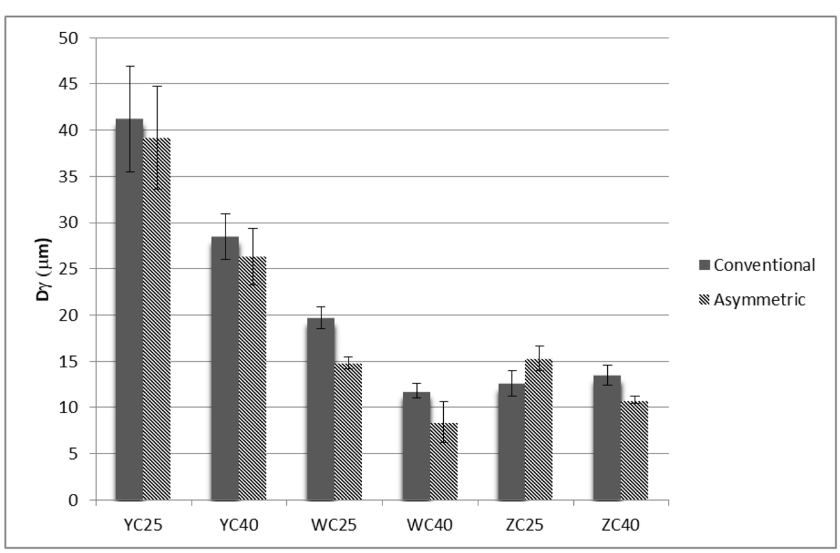


Fig. 8. PAGS resulting from each tested condition.

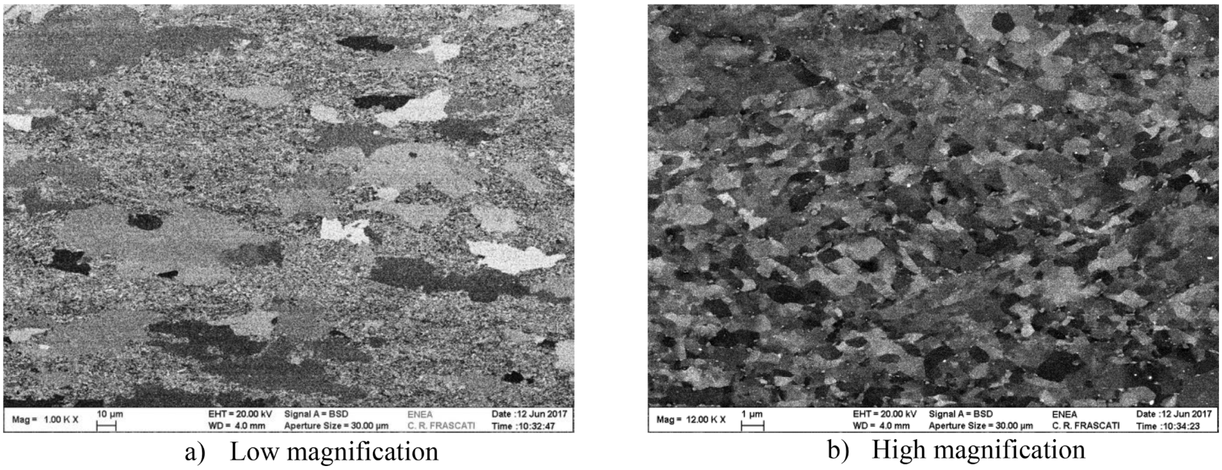


Fig. 9. FEG-SEM; Conventional cold working; tempering at 720 °C × 1 h.

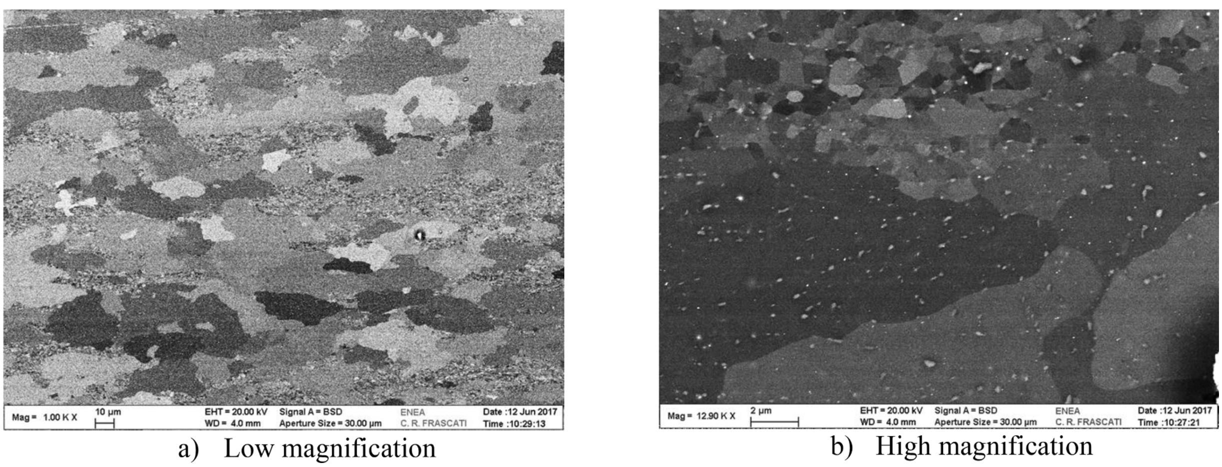


Fig. 10. FEG-SEM; Conventional cold working; tempering at 760 °C × 1 h.

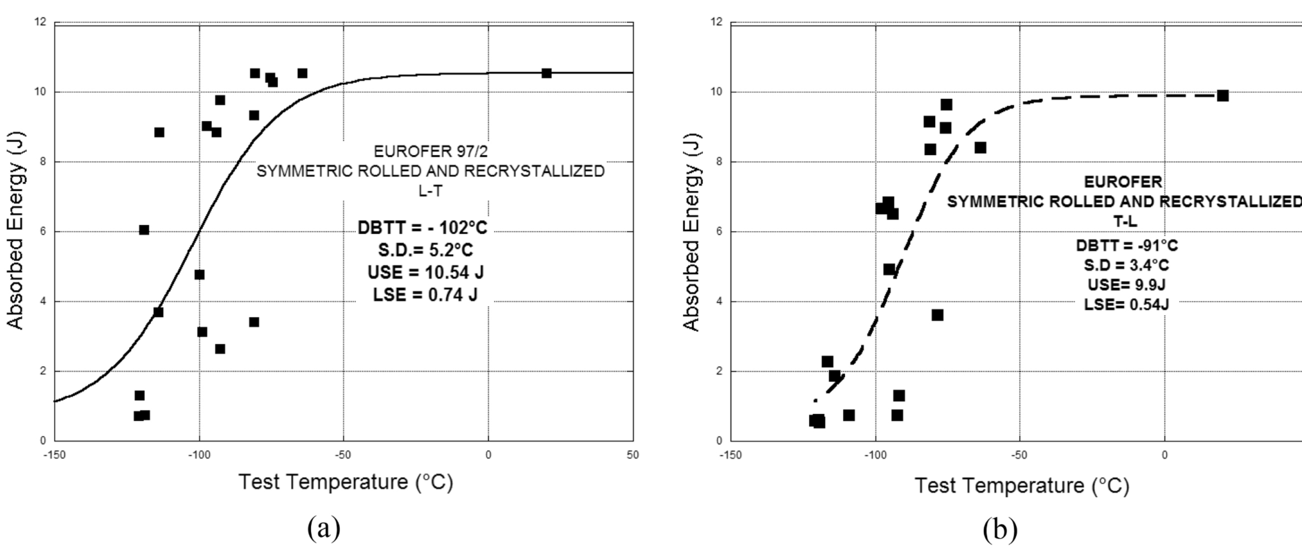


Fig. 11. KLST test results after conventional rolling on Eurofer 97/2 plate (a) L-T extraction of the specimens (b) T-L extraction of the specimens.

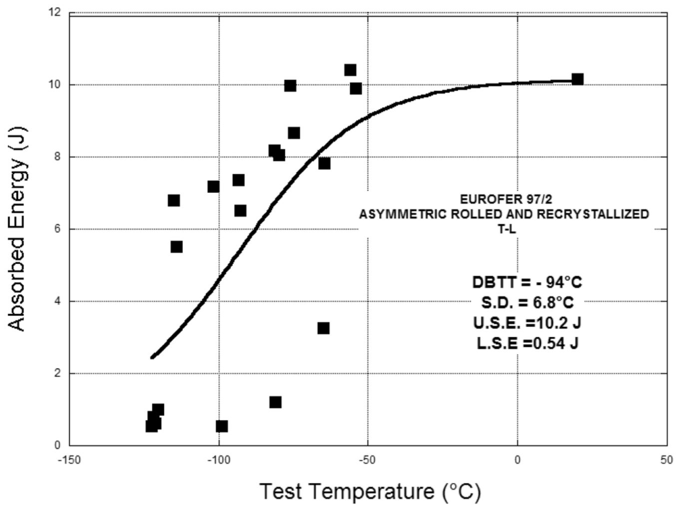


Fig. 12. KLST test results after asymmetric rolling on Eurofer 97/2 plate; T-L extraction of the specimens.

Table 5
Mean value and Standard Deviation of the results of the impact tests on KLST specimens.

Status of Eurofer 97/2	Mean value of the DBTT	Standard Deviation
Recrystallized, Symmetric Rolling, L-T extraction	−102 °C	5.2 °C
Recrystallized, Symmetric Rolling, T-L extraction	−91 °C	3.4 °C
Recrystallized, Asymmetric Rolling, T-L extraction	−94 °C	6.8 °C

excellent behaviour even if the TMT is not optimised. The comparison between Symmetric and Asymmetric cold rolling does not show substantial differences. It's reasonable to think that, as long as one will be able to achieve a completely recrystallized nanostructured microstructure, a marked decrease in the DBTT would result as a consequence.

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