Nuclear Materials and Energy 19 (2019) 79–86

Contents lists available at ScienceDirect

Nuclear Materials and Energy

journal homepage: www.elsevier.com/locate/nme

Development of innovative materials and thermal treatments for DEMO water cooled blanket

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ARTICLE INFO

Keywords:
EUROFER 97
RAFM steels
Microstructure
Heat treatment
Tensile
Charpy
KLST

ABSTRACT

One of the options currently taken into account for the realization of the first DEMO reactor is the “water-cooled lanket”. This option implies an irradiation temperature for the blanket material in the range of 280–350 °C. Therefore, in light of the under irradiation behaviour of EUROFER, namely of the DBTT shift toward high temperature due to the low irradiation temperature embrittlement, the target of the hereby reported activities is the development of much tougher alloys, to try to tolerate the embrittlement due to the low irradiation temperature. We report in this paper the work done to optimize the toughness of Eurofer 97, increasing the normalizing temperature and maintaining a small grain size using multiple normalizing treatments. We report also the mechanical behaviour of two 9Cr1WTa type alloys, produced and tested with the same aim to find alloys more resistant to embrittlement at low irradiation temperature.

1. Introduction

One of the options currently taken into account for the realization of the first DEMO reactor is 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, namely of the DBTT shift toward high temperature due to the low irradiation temperature, the target of the hereby reported activities is the development of much tougher alloys, to try to tolerate such embrittlement.

This item was addressed in several ways. The first was to study different heat treatments to increase the toughness of EUROFER 97, the second was to design alloys with different chemical composition, in order to obtain much tough materials and maintain an acceptable mechanical strength due to the low temperature operation of the blanket.

As far as Eurofer is concerned, as confirmed by the experimental data [1], it exhibits different under irradiation behaviour as a function of normalizing temperature. Eurofer normalized at 980 °C × 30 min and tempered at 750 °C × 1.5 h (EUROFER ANL in [1]) exhibits a DBTT (Ductile to Brittle Transition Temperature) (KLST specimens) of about −20 °C after irradiation of 16.3 dpa at 350 °C, while, normalized at 1050 °C × 0.5 h and tempered at 750 °C × 1.5 h and, irradiated in the same conditions, exhibits a DBTT of about −60 °C.

This behaviour seems to be confirmed by the irradiation of a 9Cr2WVTa [2] in FFTF (Fast Flux Testing Facility) reactor, normalized at 1050 °C × 1 h and tempered at 750 °C × 1 h. The DBTT of this alloy before irradiation is −88 °C and after irradiation at 365 °C to about 6.7 dpa, exhibits a DBTT shift of only 4 °C.

On the one hand, the toughness increases with the decrease of the grain size, on the other hand the better behaviour after irradiation seems to be obtained with a higher normalizing temperature. This could be due to better solutioning of primary precipitation. The goal would be to maintain a small grain size and to reduce the primary precipitation. This could be done using multiple normalizing treatments at temperatures higher than 980 °C [3–5]. Following these considerations, an experimental campaign was set up to find the best compromise between grain size and normalizing temperature. The chosen thermal treatment shifts the DBTT of KLST sample toward lower temperature of about 7 °C.

At the same time, other chemical compositions were studied, with the aims to obtain a softer alloy suitable for “water-cooled blanket”. Due to the low temperature operations foreseen for this blanket geometry, we designed alloys more free of secondary precipitations in order to promote the evolution of interstitial loops due to irradiation. These alloy are 9Cr1WTa type, with the suppression of vanadium and nitrogen. Tantalum is retained to control the grain size via the precipitation of tantalum carbide at high temperature. One of these alloys

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https://doi.org/10.1016/j.nme.2019.01.026
Received 29 November 2017; Received in revised form 25 September 2018; Accepted 27 January 2019

Table 1
Results studies on some grains distribution.

Normalizing Temperature (°C)	1th normalizing D (μm)	S.D (μm)	2nd normalizing D (μm)	S.D (μm)	3rd normalizing D (μm)	S.D (μm)
1010	10.1	4.1	8.8	4.1	7.6	3.6
1020	12.4	5.0	8.8	3.8	10.6	4.1
1030	11.0	4.9	10.0	3.9	11.6	5.0

Table 2
Best-fit parameters.

Alloy	U.S.E.(J)	L.S.E.(J)	DBTT(°C)	S.D. (°C)
As received Eurofer	9.34	0.46	−111	2
Double normalized Eurofer	9.98	0.48	−117	2

exhibits a very low DBTT (Charpy-ISO V and KLST) and sufficient mechanical strength.

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 (9Cr-0.11C-0.5Mn-0.2V-0.12Ta-0.02 N) have been normalized for 30 min up to three times at the following temperature: 1000 °C, 1010 °C, 1020 °C, 1030 °C and 1040 °C.

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 via Charpy Iso-V test and KLST test.

KLST specimens were extracted in Longitudinal-Transverse (L-T) and T-L directions respect to the rolling direction.

2.2. New alloys

After an alloying design step, two casts of about 80 kg were produced by Vacuum Induction Melting (VIM) process. The casts were hot rolled down to a thickness of about 30 mm. Several thermal treatments on small specimens were performed to determine minimum grain size and optimum tempering process. The resulting plates were thermally treated. Charpy Iso-V tests, KLST tests and tensile tests were performed.

Charpy Iso-V specimens were tested with a 300 J pendulum, KLST specimens were tested with a 25 Joule mini pendulum, and tensile tests were carried out with a 50 kN electromechanical testing machine. Tables 1, 2, 3.

3. Results

3.1. Multiple normalizing treatments on EUROFER 97/2

The microstructure of the as-received plate of Eurofer 97/2 was extremely inhomogeneous due to the presence of a relevant number of very coarse grains. Moreover the microstructure consisted of big grains and very small ones.

(Fig. 1a, b, Fig. 2a, b)

In principle, it is possible to control the grain size and recrystallization process in martensitic alloys via a cold working followed by an appropriate thermal treatment [6]. This possibility is due to the high dislocation density generated by the cold working. In martensitic alloys, the high dislocation density is due to the martensitic transformation itself. Moreover, the recrystallization process starts from the old grain boundaries. Therefore, it is possible to try to control, to refine the grain size and to increase the microstructural homogeneity by performing a certain number of multiple normalizing. The effect of multiple normalizing treatments was studied in detail in the past [4] on Ti-containing Reduced Activation Ferritic Martensitic steels (RAFMs) where the titanium concentration was about 0.1%. We observed a drastic reduction in grain size passing from a single to a double normalizing treatment with a consequent increase in toughness. Moreover, studying the grains distributions, we observed that grains distribution obtained after a double normalizing treatment were much sharper than distribution obtained from a single normalizing treatment. We had in mind the fact that Ti concentration was about four times the equivalent Ta concentration (in atomic%) and that the amount of primary precipitation could play a certain role in this grain refinement process.

Therefore, we studied the effects of this typical thermal treatment on Eurofer 97/2 with two aims: The first was to try to reduce the inhomogeneities in starting plate, and the second was to obtain a reduction in grain size and a more peaked distribution at an higher normalizing temperature.

Consequently specimens of about 2 × 2 × 2 cm of 25 mm plate have been normalized for 30 min up to three times at the following temperature: 1000 °C, 1010 °C, 1020 °C, 1030 °C and 1040 °C.

To identify the Prior Austenite Grains (PAGs), the samples were tempered at 580 °C × 1 h and chemically etched. At first, the PAGs were manually encircled on a printed photograph and the size was measured by the intercept method. Subsequently, we obtained the grains size distribution using the ImageJ free software [7]. In this case, the grain diameter was obtained as the diameter of the area of equivalent circle.

After the first normalizing treatment and, subsequently, after the second, we observed the absence of coarse grains (Fig. 3).

The double normalization treatment appears successful in achieving a slight grain refinement at each tested temperature (about 20%); some examples of the obtained microstructure and related grain size mean dimension are reported in the following figure.

In the following, we show the results (mean diameter and Standard deviation) regarding the grain size distributions and an example of the used method.

We show in the following figure the results of various multi-normalizing treatment, Charpy-ISO V and KLST tests.

The results show that the beneficial effect of a multi-normalizing treatment: although the gain in grain size reduction is not so big, the mean grain size decreases with a double normalizing treatment; moreover the standard deviation decreases as well: this implies that this treatment increases the microstructural homogeneity. The mean grain size increases or remains stable with the third normalizing treatment at temperature higher than or equal to 1020 °C. Therefore, we chose as reference treatment the following: 1020 °C × 0.5 h + a.c. + 1020 °C × 0.5 h + a.c. + 760 °C × 1.5 h as the maximum normalizing temperature with a grain size less than or equal to 10 μm. Here a.c. means air cooling. We report in the following

Table 3
Chemical compositions of new alloys (in weight%).

Alloy	Cr	W	Si	Mn	Ta	V	C	N	P	S
Eurofer 97/2(*)	8.95	1.08	_	0.55	0.12	0.2	0.11	0.022	0.0011	0.01
VM2897	9.04	0,99	0.037	0.11	0.092	< 0.03	0.092	0.0024	< 0.005	0.001
VM2898	8.95	0.99	0.044	0.11	0.04	< 0.03	0.060	0.0040	< 0.005	0.0015

(*) FZK-internal report.

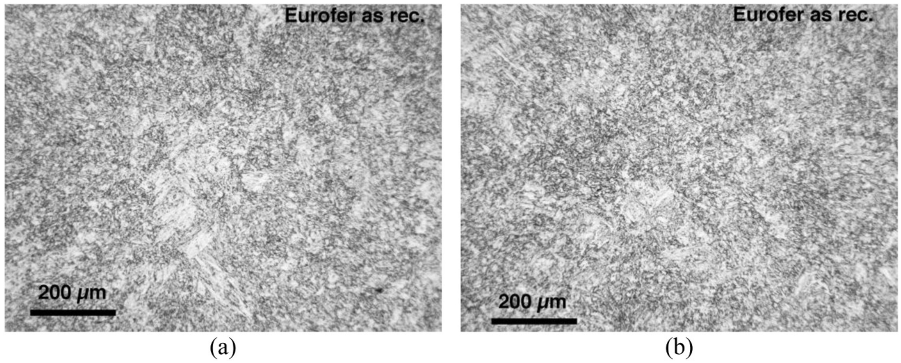


Fig. 1. a, b - Microstructural inhomogeneity of as-received Eurofer 97/2: note the presence of coarse grains.

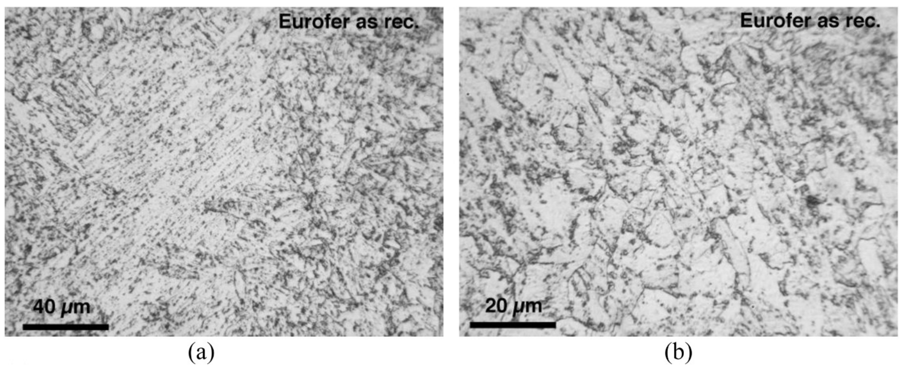


Fig. 2. a, b - Microstructural inhomogeneity of as-received Eurofer 97/2: note the simultaneous presence of big grains and very small ones.

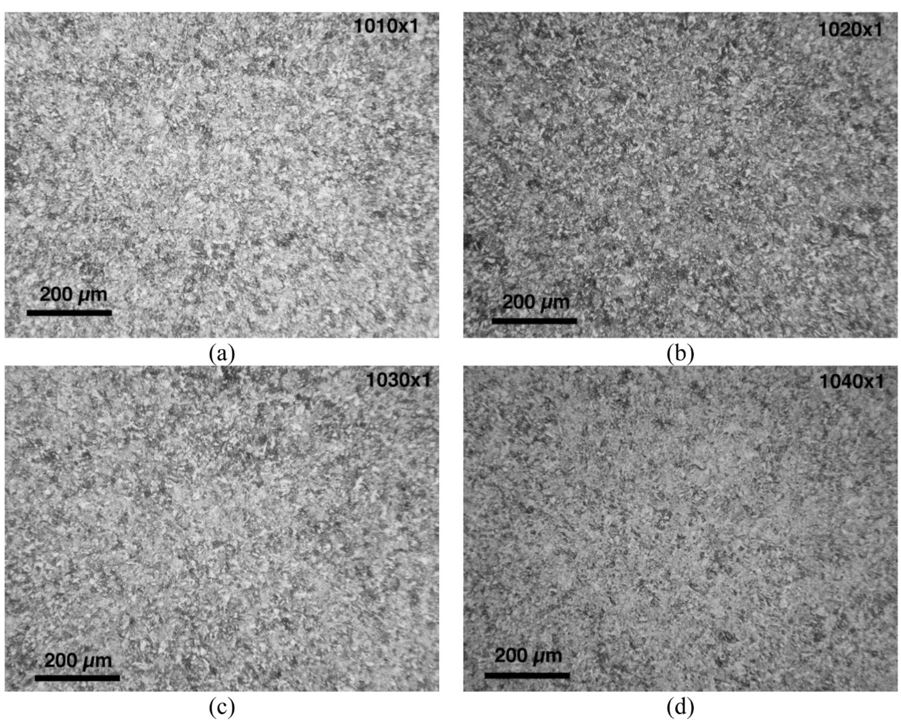
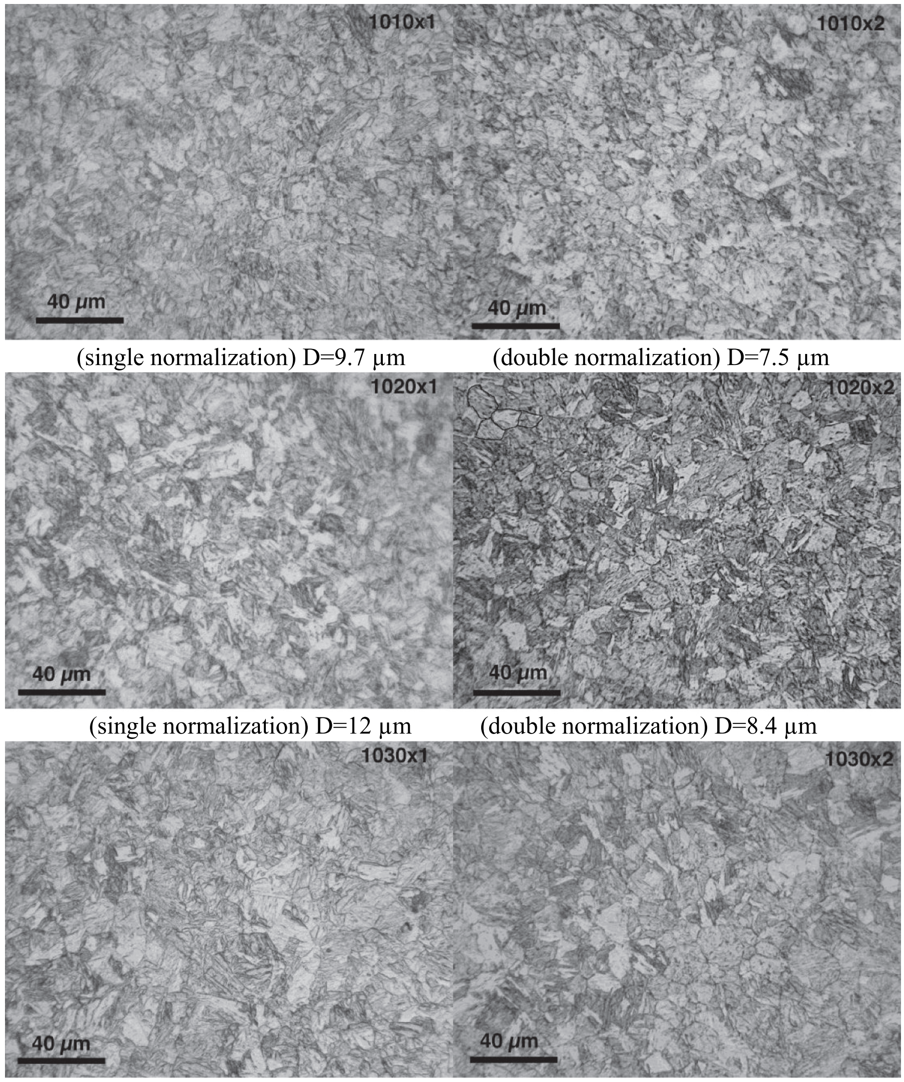


Fig. 3. Low magnification optical micrographs of some sample after the first normalizing treatment: (a) 1010 °C; (b) 1020 °C; (c) 1030 °C and (d) 1040 °C.

figure the results of Charpy-Iso V (10 mm × 10 mm) and KLST impact tests. (Fig. 6a,b, Fig. 7a,b)

Regarding the CHARPY-ISO V results, the adopted treatment reduces the DBTT of about 12 °C (from −70 °C of Eurofer 97/1 to −82 °C). Concerning the KLST tests, 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 curve exhibits a smoother behaviour. We report in the following table the values of DBTT and the Standard Deviation coming out from the best fit obtained using the standard software Keleidagraph [9].

Where U.S.E is the Upper Shelf Energy and L.S.E. is the Lower Shelf Energy. The standard deviation S.D. calculated by the software was the



(single normalization) D=9.7 μm (double normalization) D=7.5 μm

(single normalization) D=12 μm (double normalization) D=8.4 μm

(single normalization) D=12.5 μm (double normalization) D=10.5 μm

Fig. 4. Microstructure of Eurofer (and related grain size mean dimension by the intercept method) normalized once and twice at 1010 °C, 1020 °C and 1030 °C.

same for both tested alloys, i.e. 2 °C. The best fit was obtained from the following formulation: Absorbed Energy (J) = $(\mathrm{U.S.}E + L.\mathrm{S.E})/2 - (\mathrm{U.S.E} - \mathrm{L.S.E})/2 * \mathrm{Tanh}[(T(^{\circ}C) - T_0(^{\circ}C))/B]$, where T_0(°C) is the DBTT. The U.S.E and L.S.E. were previously obtained as the mean of higher values and lower values of absorbed energy, respectively. Figs. 4, 5, 8, 12, 13, 14.

Double-normalized Eurofer seems to exhibit a greater scatter of data than as received Eurofer, despite the same S.D.; but this could be due to different number of tests (namely, about 10 tests for As received Eurofer and about 30 for Double-normalized Eurofer). The behaviour of two alloys can be considered as different with a confidence limit of 80%. In any case, with a statistic of three samples for each temperature and Charpy-Iso V 10 mm × 10 mm, that is usually used to determine with a sufficient accuracy the DBTT of ferritic martensitic alloys as required by the ASTM standard E23 [10], the scatter of the data of a sufficiently homogeneous alloy is considerably reduced. A certain scatter can be observed in the transition region. For KLST sample, with the same statistic (three samples for each temperature) the scatter of data is higher than that of 10mmx10mm Charpy because the specimen region interested by the fracture is less extended than the Charpy one, so that bigger samples are less sensitive to small inhomogeneities.

3.2. *New high toughness alloys*

Two chemical compositions different from the EUROFER 97 one were theoretically defined using Thermocalc and JMATpro software. Due to the low temperature application of these two alloys (280–350 °C), we chose to investigate alloys with reduced amount of secondary precipitation, reducing the Nitrogen content and suppressing the Vanadium content. So the proposed alloys were 9Cr1WTa type with a limited amount of Carbon. The Tantalum was included into chemical composition to control the grain size.

Here we report Thermocalc calculations regarding the two chemical compositions.

Thermodynamic diagrams are quite similar except for the tantalum carbide amount and the appearance of hexagonal tantalum nitrides and chromium nitrides in alloy VM2898 due to the lower carbon content and a slight increase in nitrogen.

First study on normalizing temperature showed that these alloys exhibited grain sizes higher than those of Eurofer 97/2 due to the reduction of V and N amount, and a lower amount of carbon and tantalum respect to Eurofer 97/2 (Fig. 9–10).

The characterization of these alloys was then completed performing Continuous Cooling Transformation (CCT) diagrams (Fig. 11a,b).

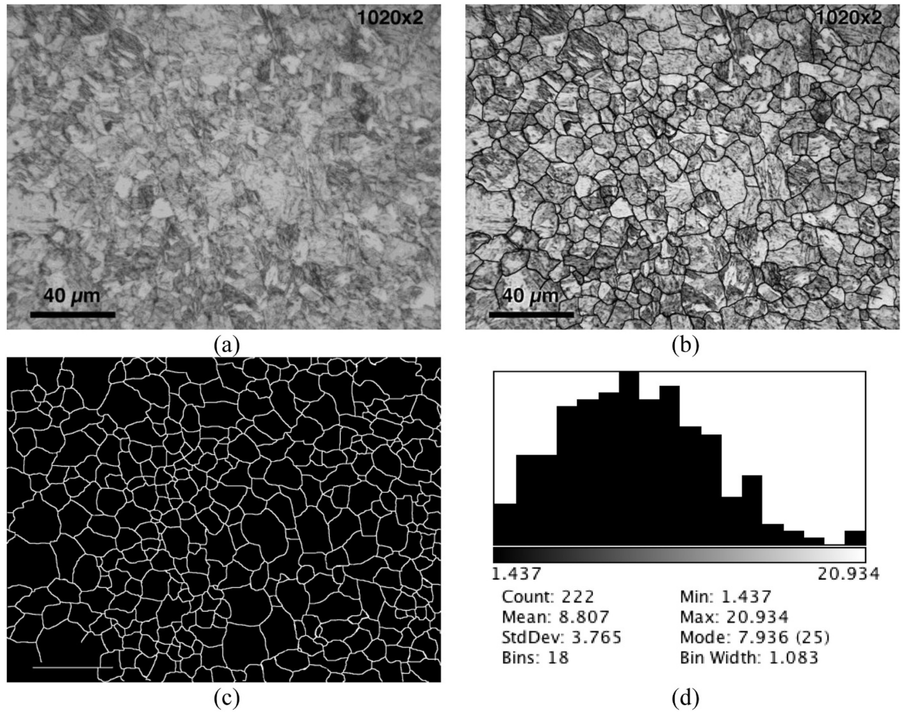


Fig. 5. Description of the used method to obtain the grains distribution on Eurofer 97/2 normalized two times at 1020 °C × 0.5 h: (a) original micrograph; (b) grain contouring; (c) binarization; (d) diameter distribution.

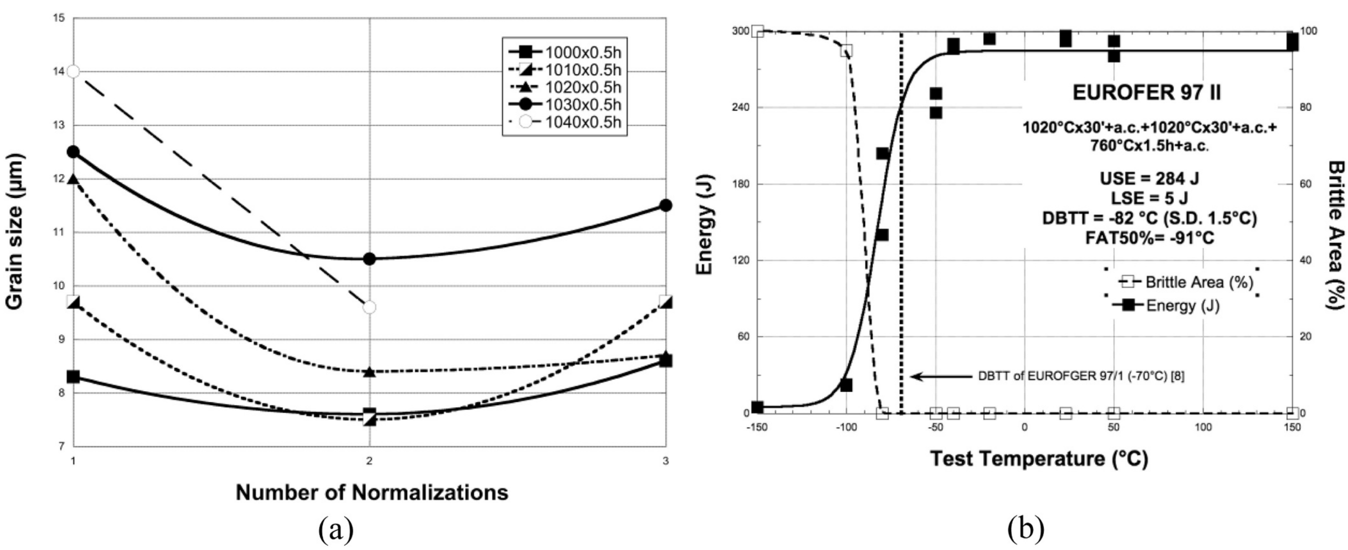


Fig. 6. (a) Grain size behaviour as a function of the number of normalizing treatments; (b) Charpy-ISO V results of selected thermal treatment.

Taking into account the beneficial effect of double normalizing treatment observed in Eurofer 97/2, we decided to perform the following double normalizing treatment for both alloys at a normalizing temperature just over Ac_3: 920 °C × 1.5 h + $a.c$ + 920 °C × 1.5 h + a.c. The tempering treatment was chosen in order to have a hardness of about 200 Kg/mm^2 corresponding to an UTS of about 600 MPa, i.e. 760 °C × 1 h.

Here we report the results of mechanical test regarding Charpy ISO-V 10 mm × 10 mm, KLST impact tests and tensile tests.

Comparing the Yield Stress (YS) curves, the new alloys are less resistant than Eurofer 97, as expected. The difference in YS and Ultimate Tensile Strength (UTS) at room temperature is in the order of 100 MPa (from about 540 MPa down to 460 MPa for the YS and from about 650 Mpa down to 580 MPa). This difference goes down as the temperature increases. At 500 °C this difference is in the order of 10 MPa and 20 MPa, for YS and UTS respectively.

Regarding the Ductility, on the contrary, the Uniform elongation of new alloys are higher than the Eurofer one while the Total elongation behaves in a different way: Alloy VM2897 (0.1%C, 0.1%Ta alloy) is the most ductile respect to the other two up to 400 °C. Over this temperature the trend is inverted and Eurofer alloy exhibits the greatest ductility.

Alloy VM2898 (0.06%C, 0.04%Ta) exhibits the lowest Total Elongation at all over the temperature range.

Charpy Iso V results are summarized in the following figure.

Alloy VM2897 exhibits the best behaviour with the highest U.S.E and the lower DBTT (−86 °C). Compared with Optimized Eurofer 97/2 described in the previous paragraph, the behaviours are quite similar

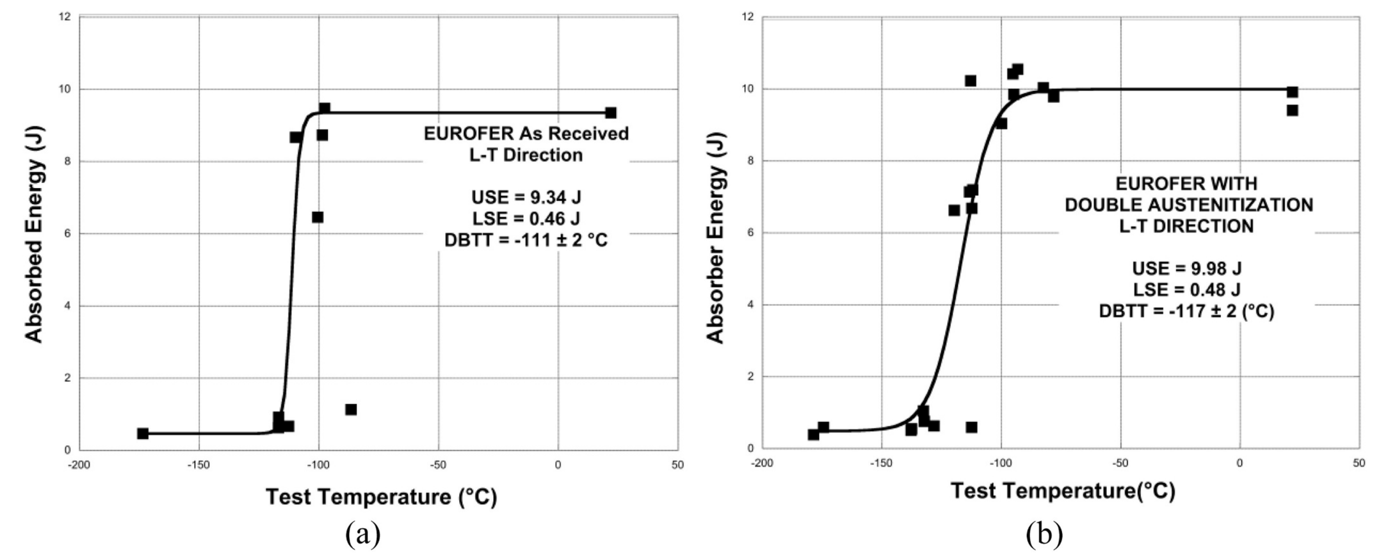


Fig. 7. KLST test results on Eurofer 97 II Heat 993,391 (a) in the as received conditions and (b) after double normalization at 1020 °C × 0.5 h and tempering at 760 °C × 1.5 h.

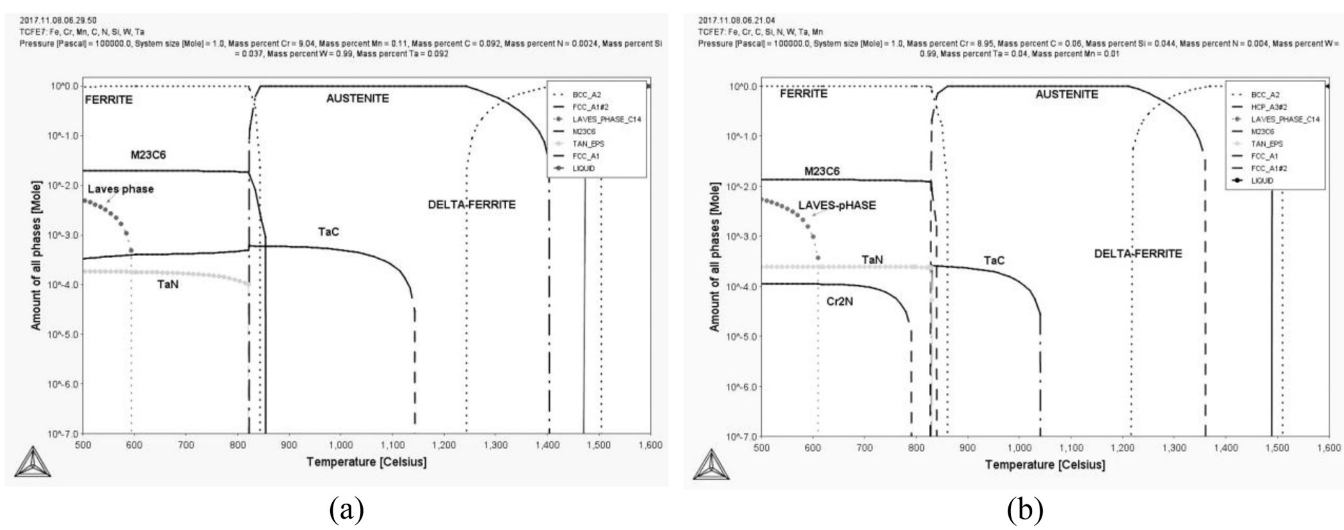


Fig. 8. Phases stability diagrams according to Thermocalc results for alloy VM2897 and VM2898.

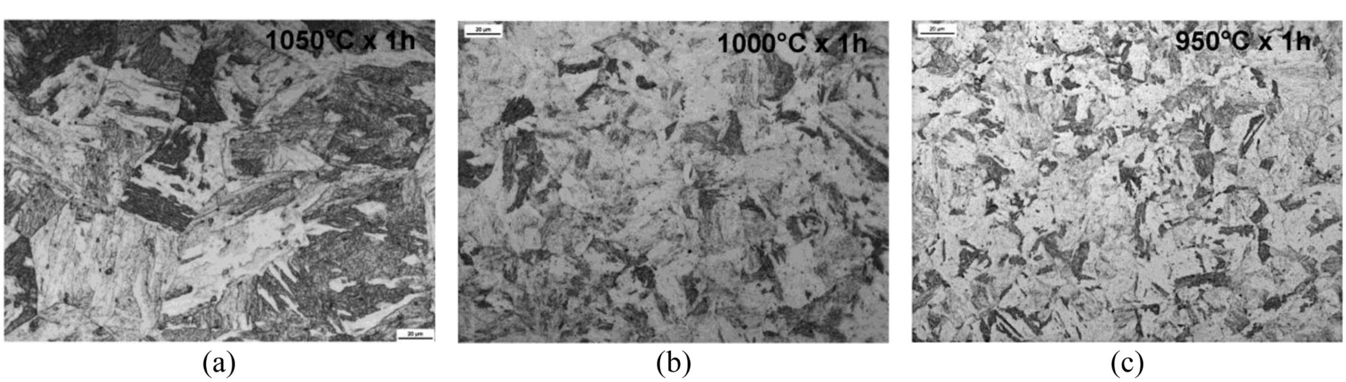
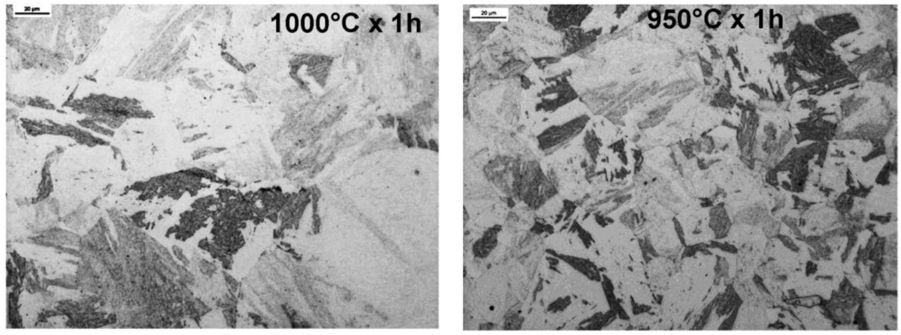
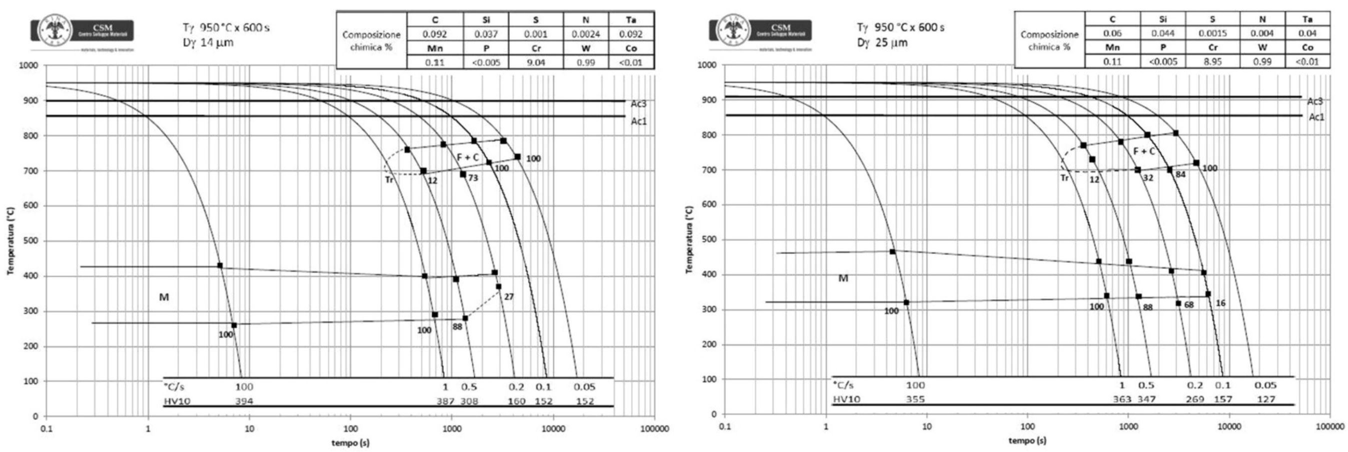


Fig. 9. Preliminary studies to determine the PAGs as a function of normalizing temperature for VM2897: (a) 1050 °C × 1h; (b) 1000 °C × 1h; (c) 950 °C × 1 h. The PAGs ranges qualitatively from about 70 µm to about 25 µm.



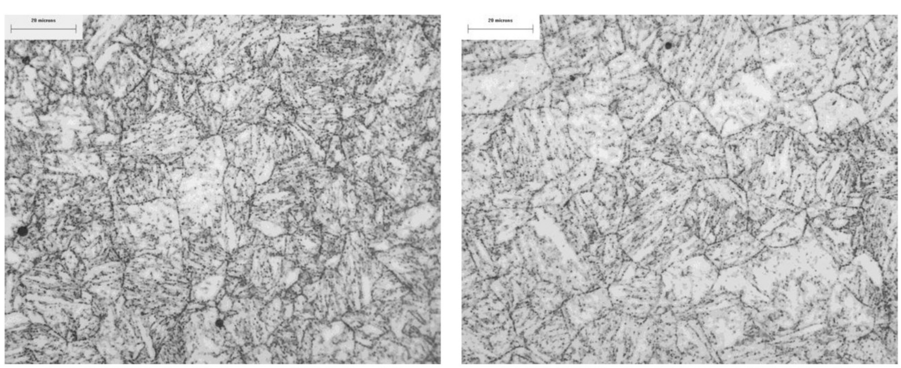
(a) (b)

Fig. 10. Preliminary studies to determine the PAGS as a function of normalizing temperature for VM2898: (a) 1000 °C × 1h; (b) 950 °C × 1 h. The PAGS ranges qualitatively from about more than 100 μm to about 40–50 μm.



(a) (b)

Fig. 11. CCT diagrams of (a) VM2897 and (b) VM2898; Ac_3 is about 900 °C; critical velocity is about 1 °C/s for both alloys.



(a) VM2897- d = 20.3 mm ASTM G = 7.9 (b) VM2898- d = 22.2 m ASTM G = 7.7

Fig. 12. Optical metallography of normalized alloys: (a)VM2897; (b) VM2898.

but the transition of Alloy VM2897 is steeper than the Optimized Eurofer 97/2, indicating a more homogeneous microstructure.

4. Conclusions

- Several thermal treatments were conducted on Eurofer 97/2 alloy to try to increase the toughness at the increasing normalizing temperature. The obtained results indicate that the chosen thermal treatment consisting in a double normalizing at 1020 °C × 0.5 h and standard tempering at 760 °C × 1.5 h increases the toughness of Eurofer 97 by shifting the DBTT of about −7 °C towards the lowest temperatures (KLST samples).
- Two new alloys, 9Cr-1W-0.1C-0.1Ta and 9Cr-1W-0.06C-0.04Ta type were produced and studied, to reduce the overall secondary precipitation during tempering, with the aim to foster the evolution of dislocation loops created by low temperature irradiation and to reduce the low temperature irradiation hardening.
- The alloy VM 2897 exhibits the better behaviour as far as the

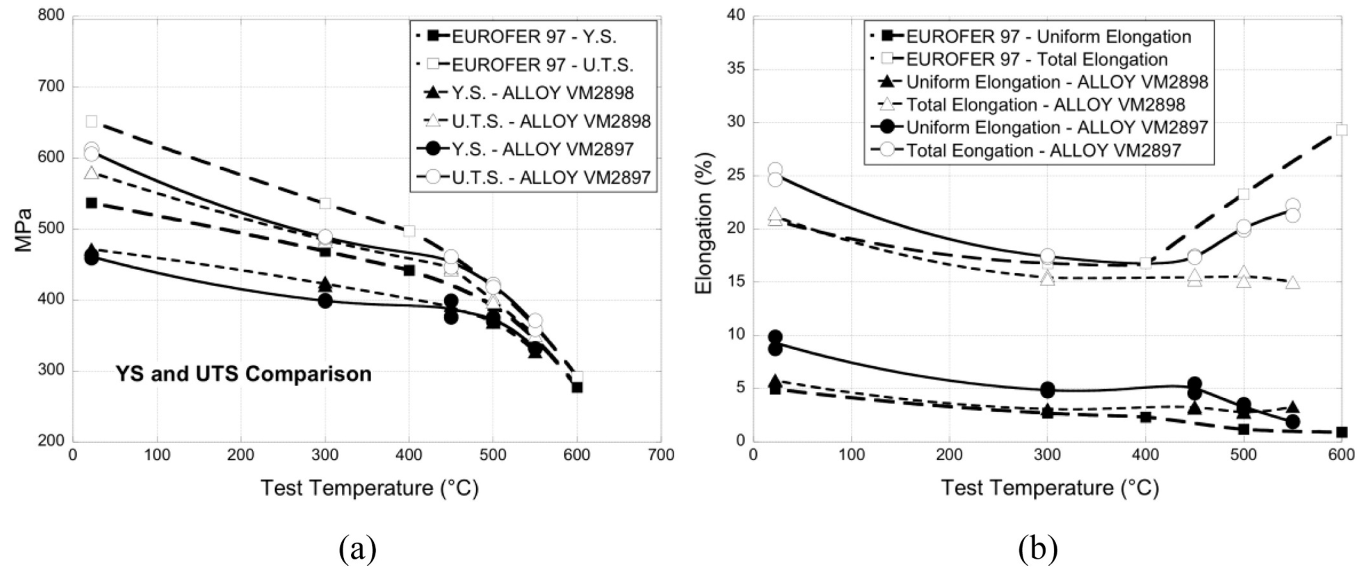


Fig. 13. Mechanical properties of Alloys VM2897 and VM2898. Comparison with EUROFER 97 [6]: (a) YS and UTS comparison; (b) uniform and total elongation comparison.

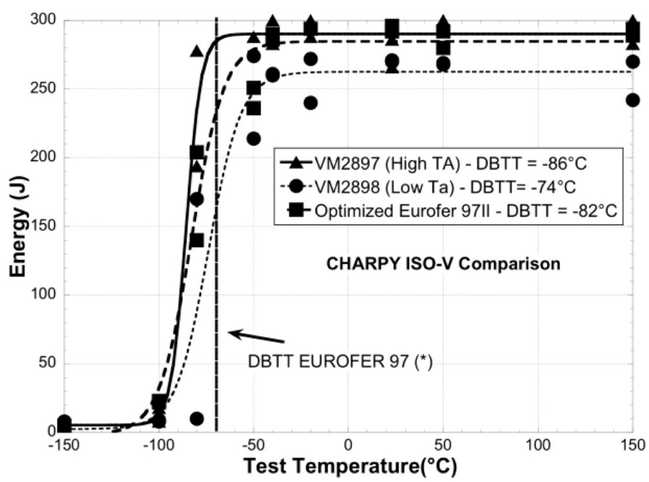


Fig. 14. Charpy ISO V results. Comparison between new alloys and optimized Eurofer 97/2. The vertical line (*) indicates the DBTT values of Eurofer standard as reported in [8].

toughness is concerned, while the mechanical properties remain acceptable due to the possible low temperature application of this alloy.

Acknowledgement

This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014–2018 under grant agreement No 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

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