Optimisation of production method of a nanostructured ODS ferritic steels

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Abstract. This work aims at improvement of plasticity of an yttria-reinforced Fe-14Cr-2W-0.3Ti ODS ferritic alloy as compared to the previously fabricated and HIP-ed ODS alloy with the same nominal composition. Two modifications in the production route of an ODSFS were proposed to improve their mechanical properties. The first way was applying of multiple hot-cross rolling passes at various degrees of deformations. This resulted in an increase of total and uniform elongations after applying reduction of thickness (ROT) of 65% and 80% and a decrease of DBTT below room temperature. Second way was to replace the elemental powders by a pre-alloyed Ar atomized powder particles which allowed for shorter milling time and thus lower O₂ and N₂ contamination in the powders and also in the consolidated steel. The impact tests showed slightly lower DBTT of the cross-hot rolled ODS steel samples produced from pre-alloyed powder.

1. Introduction

Oxide dispersion strengthened (ODS) reduced activation ferritic (RAF) steels are promising candidate materials for first wall and breeding blanket applications in the future fusion reactors. These materials are attractive due to their excellent high temperature mechanical properties and good resistance to neutron irradiation [1–7].

RAF ODS steels contain the following elements in an iron matrix: chromium (14%) which provides stability of the ferritic structure, causes solid solution hardening and corrosion resistance, tungsten which contributes to solid solution hardening and improves the thermal stability of the alloy, and small amounts (∼0.3%) of titanium and yttrium forming nano-oxides which improve the steel resistance to creep, fatigue and radiation damage.

The production of nano-structured ODS ferritic steels usually involves powder metallurgical methods including mechanical alloying and subsequent powder compaction using either hot extrusion (HE) [4] or hot isostatic pressing (HIP) [8,9]. HIP usually yields a more isotropic microstructure but a lower ductility and fracture toughness as compared to the materials produced by HE [10].

2. Methodology

The first stage of the powder metallurgy route for ODS steel production consists of preparing powders mixtures with the proportions corresponding to the final composition in a glove-box
with Ar atmosphere, then transferring the powder mixtures into the attritor in container filled
with Ar, milling of powders in a gas tight chamber and its discharging afterwards in a
protective atmosphere. Our previous results [11,12] indicated that the use of hydrogen as
milling atmosphere can lead to improved plasticity of the steel by reducing powders oxidation
and preventing trapping of Ar gas in the steel particles during mechanical alloying. In this
work the powders were milled in attritor at controlled H\textsubscript{2} pressure using the following
parameters: cycles of 1min at 750 and 1min at 380 rpm for total time of 80h in the case of the
elemental powder and 8h for the mixtures of pre-alloyed powder and reinforcement particles.
The optimum milling times were selected by SEM observations and XRD tests. Dissolution
of the alloying elements was observed in the first case and an uniform distribution of oxide
nano-particles in the second. The contamination of powders with oxygen and nitrogen was
characterized by an inert gas fusion method for two types of ODS powders mixtures at
various milling times (see Table 1).

Much lower oxygen and nitrogen levels can be noticed in the case of the pre-alloyed Ar-
atomised powder than in the elemental powders with addition of 0.3 wt. % yttria particles.

| TABLE I: Concentration of oxygen and nitrogen in the powders - Criterion for selection of
substrates and milling time. E – elemental; P – pre-alloyed Fe14Cr2W0.3Ti base alloy. |
<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As mixed</td>
<td>E</td>
<td>E</td>
<td>As-mixed</td>
<td>P+0.3Y\textsubscript{2}O\textsubscript{3}</td>
</tr>
<tr>
<td></td>
<td>E+0.3Y\textsubscript{2}O\textsubscript{3}</td>
<td>+0.3Y\textsubscript{2}O\textsubscript{4}</td>
<td>+0.3Y\textsubscript{2}O\textsubscript{8}</td>
<td>8h</td>
<td>8h</td>
</tr>
<tr>
<td>wt. % O\textsubscript{2}</td>
<td>0.44</td>
<td>0.53</td>
<td>0.65</td>
<td>0.15</td>
<td>0.27</td>
</tr>
<tr>
<td>wt. % N\textsubscript{2}</td>
<td>0.04</td>
<td>0.06</td>
<td>0.06</td>
<td>0.01</td>
<td>0.06</td>
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The Hot Cross Rolling (HCR) was carried out at the CSM Center (ENEA) after HIP and
stress-relieving heat treatment at 800°C. The highest achieved degree of deformation ϕ
applied to ingots of ca. 300 g was of 80 % reduction of thickness (ROT). A single preheating
at 1100°C was followed by rolling steps at deformation degree of 5% alternately in two
perpendicular directions in the rolling plane at 800°C – and reheated to this temperature
before every rolling step. The two-directional rolling was implemented to avoid non-
uniformities in the microstructure, including an excessive texture in the rolling plane.

3. Results

3.1. Microstructures

Optical microscopy was employed for low-magnification microstructure analysis of two ODS
steels based on the elemental powders in the as-consolidated state - after HIP and after HCR
at 65% ROT. In the case of the HIP sample there are quite large oxides and pores as black
dots along the pre-particle boundaries (Fig.1a) while in the case of the hot rolled sample these
features are much finer (Fig.1b). The micro-pores are the reason of weakening the pre-particle boundaries and thus cause of the brittle behavior of the steel after HIP.
FIG. 1. Optical microscope images of electro-polished surfaces of metallographic samples of ODS FS with Y2O3 particles after (a) HIP, (b) HIP and HC-rolling.

TEM observations of the steels after HIP and after HCR showed large regions recovered from dislocations introduced by milling. The hot-cross rolling practically did not change the grain size and the average oxides particle diameter. The average grain size estimated by TEM were of 0.3 and 0.5 microns in the HIP and HCR-65% samples, respectively. The oxides particles diameter was estimated based on TEM bright field images at higher magnification (50k) of about 500 particles. The average diameter of the oxides slightly increased from 6 nm after HIP to about 10 nm after HCR in all degrees of deformation. This coarsening of oxides particles could be related to a preheating step at 1100°C close to the maximum HIPping temperature used to homogenize the composition before the rolling.

3.2. Mechanical properties

- Effect of hot-cross rolling

Charpy impact tests were done for the v-notched ODS samples (3x4x27mm) before and after hot-cross rolling for the three deformation degrees: 50, 65 and 80% and for the HIP sample: For the HIP sample the upper shelf energy values are generally very low which could indicate a relatively low toughness in the plastic fracture regime, which is characteristic for samples produced by powder metallurgy. It took about 1 J to break the samples after HIPping and after HCR at 50% ROT. The hot-cross rolled ODS steels in which 65 and 80% ROT was achieved, show higher upper shelf energy (USE) and lower transition temperature (DBTT) in comparison with the as-HIPped sample and the rolled one at 50% ROT, whereas the 80% ROT has led to the lowest DBTT of about -50°C.
FIG. 2. Charpy impact energy versus sample temperature for the as-consolidated (HIP) ODS steel samples and a series of samples having varying deformation degree (50-80%) after hot-cross rolling.

Tensile test were done using flat samples with cross section of 0.75 mm² and gauge length of 8 mm at test temperatures between 25 and 750°C. The results are summarised in Fig. 3.

A significant reduction of tensile strength was observed in the case of samples in which 50% to 65% thickness reduction was obtained, while the elongation was gradually increasing with increase of applied deformation during rolling.

A characteristic feature of the 50% and 65% - ROT samples was a smooth change of slope on the engineering strain-stress curves, compared with a rather abrupt change (strengthening degree) in HIP.

The general tendency was a decrease of UTS and YS with test temperature in the non-rolled steels and at 50% reduction of thickness, whereas at 65% and 80% much lower UTS values at RT were observed, being comparable with the ones obtained at 450°C. Samples tested at 750°C had typically UTS of about 200 MPa. Thus the effect of HCR causing the UTS and stiffness reduction is getting pronounced at above a thickness reduction of 50%, therefore the effect on improvement of Charpy impact behaviour is expected in that case.

The tensile curves obtained for the steels produced using the pre-alloyed powder showed an opposite tendency compared with the ones made using the elemental powder that is: an increase in strength and decrease in total elongation at RT after hot rolling.

In the HCR4 rolled to 65% ROT, the UTS at 450°C almost doubled while at 750°C it did not change after rolling. The total elongation of the RT-tested samples made of the pre-alloyed, higher quality material was larger by about 30% than in the case of the elemental material. This indicates a much better plasticity of the ODS containing less oxygen.

Interestingly, the tensile strength and plasticity of the PA4 material are very similar to those obtained for HCR3 – so rolling resulting in 80% thickness reduction leads to a similar response like when using a higher purity powder. This could mean that in the series of samples HCR1-3 which have the same substrate powder with higher oxygen concentration,
the present larger oxides and nitrides are probably getting refined and so do the pre-austenite grains, which substantially improves the plasticity of the steel.

**FIG. 3.** Stress-strain curves (engineering strain) at temperatures from room temperature to 750°C obtained by tensile tests of the ODS FS made using elemental powders with Y2O3 particles; (a) after HIP (b) HIP followed by HCR at 50% (c) 65% (d) 80% reduction of thickness.

**TABLE II: Results of tensile test of the as-HIPped and hot-cross rolled ODS samples at various thickness reductions made of elemental base alloy.**

<table>
<thead>
<tr>
<th>Test T (°C)</th>
<th>ROT: 0%</th>
<th>ROT: 50%</th>
<th>ROT: 65%</th>
<th>ROT: 80%</th>
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<tr>
<td></td>
<td>Rm (MPa)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>25</td>
<td>1173</td>
<td>1109</td>
<td>707</td>
<td>25</td>
</tr>
<tr>
<td>450</td>
<td>858</td>
<td>821</td>
<td>587</td>
<td>450</td>
</tr>
<tr>
<td>750</td>
<td>299</td>
<td>313</td>
<td>165</td>
<td>750</td>
</tr>
<tr>
<td></td>
<td>Rp0.2 (MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>1053</td>
<td>937</td>
<td>330</td>
<td>393</td>
</tr>
<tr>
<td>450</td>
<td>801</td>
<td>673</td>
<td>420</td>
<td>399</td>
</tr>
<tr>
<td>750</td>
<td>281</td>
<td>250</td>
<td>146</td>
<td>154</td>
</tr>
<tr>
<td>ε</td>
<td>25.000</td>
<td>0.043</td>
<td>0.037</td>
<td>0.095</td>
</tr>
<tr>
<td>εu</td>
<td>0.02</td>
<td>0.028</td>
<td>0.024</td>
<td>0.019</td>
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<tr>
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</table>
- **Effect of substrate powder purity**

Charpy test were also carried out for the as-HIPped and for HC-rolled ODS samples made of the prealloyed powder (i.e. less oxygen contamination). The hot rolled samples showed a higher USE and lower DBTT (-24°C) values than their elemental counterparts (-8°C), whereas although the USE also improvement in the case of the pre-alloyed as-HIPped samples, the DBTT was in that case worse (+59°C) than for the elemental ones (+8°C).

![Graph showing Charpy impact energy vs. temperature](image)

**FIG. 4.** Results of Charpy impact tests of v-notched samples of the prealloyed ODS ferritic steels (a) after HIP and (b) HIP followed by HCR at 65% ROT.

![Stress-strain curves](image)

**FIG. 5.** Stress-strain curves (engineering strain) at temperatures from room temperature to 750°C obtained by tensile tests of the ODS FS made using prealloyed powder with Y2O3 particles (a) HIPped samples and (b) HIP and HCR samples at 65% ROT.
TABLE III: Results of tensile test of the as-HIPped and hot-cross rolled ODS samples made of prealloyed base alloy.

<table>
<thead>
<tr>
<th>Test T (°C)</th>
<th>25</th>
<th>450</th>
<th>750</th>
<th>25</th>
<th>450</th>
<th>750</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_m) (MPa)</td>
<td>1173</td>
<td>858</td>
<td>299</td>
<td>718</td>
<td>384</td>
<td>203</td>
</tr>
<tr>
<td>(R_{p0.2}) (MPa)</td>
<td>1053</td>
<td>801</td>
<td>281</td>
<td>412</td>
<td>329</td>
<td>168</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>25.0</td>
<td>0.065</td>
<td>0.043</td>
<td>0.16</td>
<td>0.095</td>
<td>0.04</td>
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<tr>
<td>(\varepsilon_u)</td>
<td>0.02</td>
<td>0.028</td>
<td>0.024</td>
<td>0.011</td>
<td>0.021</td>
<td>0.013</td>
</tr>
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</table>

The use of elemental powders required relatively long milling time for dissolution of elements and Y2O3 in order to produce fine dispersion of Y-Ti-O nanoclusters. On the other hand, this has lead to a significant contamination with elements from atmosphere but also from the mill debris (EDS of the steel after MA for 80 h showing presence of Si in the precipitates, most likely from the steel of the drum and the balls). As a way to avoid prolonged milling time, the elemental powders mixtures were substituted by an Ar-atomised, pre-alloyed powder (Fe-14Cr-2W-0.3Ti), which allowed using shorter milling time (between 8 and 40 h instead of 80 h). This has lead to lowering the oxygen content in the as-mechanically alloyed powder but at the same time a sufficiently uniform distribution of oxides was achieved.

4. Conclusions

Precipitation strengthening by addition of fine oxide particles and transformation (HIP) induced stress are the main cause of high tensile strength and stiffness of the as-HIPped ODS ferritic steels. On the other hand, weak cohesion forces between the pre-particle grains due to either non-homogeneous distribution of alloying elements but mainly because of larger oxides and nitrides at the pre-particle boundaries lead to lower fracture toughness and in consequence, to a brittle fracture mode in these composites.

In order to avoid typical for the ODS steels brittle fracturing, a thermal-mechanical treatment was applied in the current work, which allowed enhancement of the plasticity of these alloys. The multiple hot cross rolling allowed achieving desired deformation steps and rolling the samples in two perpendicular directions, which minimized the structure anisotropy in the rolling plane. The improvement of plastic yield in the hot rolled samples was related most probably to a decrease of the remnant porosity but also due to an extensive structure recovery which was evident from the microscopic observations which revealed: smaller micro-porosity and much smaller dislocation density especially in the case of 65% deformation. The TEM observations also brought about grain elongation in the plane perpendicular to the rolling plane at 80% deformation, insignificant changes in grain size and some coarsening of the oxides nanoparticles with increasing degree of deformation.

The Charpy test showed a significant reduction of DBTT transition temperature and an increase of the upper shelf energy when the deformation was 65% of thickness or higher. The tensile test in all hot rolled steel samples showed a decrease in tensile strength and yield stress along with increase of plastic strain. An additional improvement of plasticity was achieved by using the pre-alloyed powder instead of a mixture of elemental powders.
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References