SANS study of microstructural evolution in oxide strengthened EUROFER steel after heat treatments

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Abstract. Oxide dispersion strengthened (ODS) reduced activation ferritic/martensitic steels are being developed for structural applications in future fusion reactors since they would allow consistently increasing the operation temperature. The 9%CrWVTa Eurofer-97 steel has been selected as a base material strengthened by Y₂O₃ contents of 0.3 and 0.5 wt% and produced in a powdermetallurgical route by mechanical alloying and hot isostatic pressing (HIP). The mechanical properties are strongly correlated with Y₂O₃ particle average size and spatial distribution, therefore small-angle neutron scattering (SANS) is quite useful to investigate how these evolve in the course of the production steps. Solid polycrystalline samples as well as mechanically alloyed powders have been investigated after thermal treatments thus simulating the HIP conditions. The obtained SANS results show that annealing at high temperature results in a redistribution of scattering centres sizes, which might be attributed to the growth of small Yttria particles and possibly of larger carbides.

1. Introduction

Oxide dispersion strengthened (ODS) reduced activation ferritic/martensitic steels are attractive candidates for structural applications in future fusion reactors since they would allow increasing the operation temperature by approximately 100°C, with a consequent improvement of the reactor efficiency [1]. The 9%CrWVTa Eurofer-97 steel (8.9 Cr, 1.1 W, 0.2 V, 0.14 Ta, 0.42 Mn, 0.11 C wt%) has been selected as a base material strengthened by Y₂O₃ contents of 0.3 and 0.5 wt% and produced in a powdermetallurgical route by mechanical alloying and hot isostatic pressing. ODS Eurofer-97 steel was produced by inert gas atomisation of the base material and subsequent mechanical alloying in industrial ball mills; hot isostatic pressing was then chosen as the appropriate consolidation process [2]. The internal structure of the ODS particles in consolidated materials has been studied by analytical transmission electron microscopy (TEM) applying microanalytical techniques (EDS and EELS, Ref. [3]) but a direct observation of these nano-particles by TEM in mechanically alloyed powders has not been possible until now because of difficulties in preparing the specimens for such observations. Small-angle neutron scattering (SANS) has therefore been utilized to
investigate how these nano-sized particles evolve under isochronal annealing thus simulating the thermal conditions during the HIP process. Previous SANS measurements [4] carried out on polycrystalline ODS Eurofer-97 with the same chemical composition as the one investigated in this study, have in fact shown the usefulness of this technique to characterize Y$_2$O$_3$ particle average size and distribution, obtaining results in good agreement with TEM and relevant to understand the changes in the mechanical properties, which are strongly correlated with such a distribution.

2. Experimental technique and results
The investigated samples were mechanically alloyed powders of ODS Eurofer-97 steel and Yttria (0.5 wt%) in the as-received state, annealed 2 h at 750°C and annealed 2 h at 1100°C in vacuum. It is supposed that in this temperature range the Y$_2$O$_3$ particles will evolve and may change their size distribution and new phases, such as carbides, may nucleate. The SANS measurements were carried out at the D22 instrument at the High Flux Reactor of the Institut Max von Laue - Paul Langevin, Grenoble. A sample-to-detector distance of 2.00 m with a wavelength, $\lambda$, of 6 Å were used. Defining the modulus of the scattering vector $Q = \frac{4\pi \sin \theta}{\lambda}$ (where $2\theta$ is the full scattering angle), these experimental conditions gave a $Q$ interval ranging from 0.02 to 0.3 Å$^{-1}$, which corresponds to particle sizes ranging from 10 to 300 Å approximately.

![Figure 1. Nuclear SANS cross-sections of Eurofer-97 ODS powders reference mechanically alloyed (squares), mechanically alloyed plus annealed at 750°C (circles) and at 1100°C (triangles); the experimental errors range from 5 to 10%.

The powders were placed in a quartz cell 1 mm thick and the empty quartz cell was used as a reference for the background. Calibration to absolute SANS cross-section (expressed in cm$^{-1}$ sterad$^{-1}$) was obtained by measurement of water in a quartz cell; the data were treated by the ILL standard programs [5]. A horizontal magnetic field was applied perpendicular to the incoming neutron beam in order to fully align the magnetic moments in the sample. Thus only nuclear scattering occurs in the horizontal plane, while nuclear and magnetic scattering occur in the vertical one. The purely magnetic scattering is obtained as the difference between the vertical and horizontal SANS cross-sections. In fact, in the case of magnetic samples, the total SANS cross-section $\frac{d\Sigma(Q)}{d\Omega}$ (where $\Omega$ stands for the solid angle) can be written as the sum of two terms

$$\frac{d\Sigma(Q)}{d\Omega} = \left(\frac{d\Sigma(Q)}{d\Omega}\right)_{nuc} + \left(\frac{d\Sigma(Q)}{d\Omega}\right)_{mag} \sin^2 \alpha$$

(1)
where $\alpha$ is the azimutal angle on the detector plane. The ratio of the “vertical” to the “horizontal” SANS components:

$$R(Q) = \frac{\frac{d\Sigma(Q)}{d\Omega}_{\text{nuc}} + \frac{d\Sigma(Q)}{d\Omega}_{\text{mag}}}{\frac{d\Sigma(Q)}{d\Omega}_{\text{nuc}} + \frac{d\Sigma(Q)}{d\Omega}_{\text{mag}}} = 1 + \frac{(\Delta\rho)^2_{\text{mag}}}{(\Delta\rho)^2_{\text{nuc}}}$$  \hspace{1cm} (2)

is related to the composition of the microstructural inhomogeneities and its dependence on $Q$ implies that defects of different size or composition are present in the investigated sample, $(\Delta\rho)^2$ being the “contrast” or square difference in neutron scattering length density (nuclear and magnetic respectively) between the observed nuclear and magnetic inhomogeneities and the matrix. However, as in the previous study of ref. [4], no difference was found in the Q-dependence between nuclear and magnetic scattering, i.e. nuclear and magnetic inhomogeneities are of the same sizes.

The SANS nuclear and magnetic cross-sections can each one be written as

$$\frac{d\Sigma(Q)}{d\Omega} = (\Delta\rho)^2 \int_0^\infty dR N(R) V^2(R) \left| F(Q, R) \right|^2$$  \hspace{1cm} (3)

where $N(R)$ is the number per unit volume of centers with a typical size between $R$ and $R+dR$, $V$ their volume and $\left| F(Q, R) \right|^2$ their form factor (assumed to be spherical in the present case) and $(\Delta\rho)^2$ is the nuclear or magnetic “contrast”. The volume distribution function is defined as:

$$D(R) = N(R) R^3$$  \hspace{1cm} (4).

$N(R)$ was determined, by transformation of eq. (3), using the method described by in [6] and more recently discussed in [7]. This code assumes that the size distribution function can be described by a set of cubic B-spline functions, with equispaced knots in log $R$ scale. The number of splines is determined by the $R$-range where the size distribution is to be explored (always larger than the range where different sizes can be effectively resolved) and by the required degree of detail. The logarithmic representation of $N(R)$ is quite suited for the case of technical alloys, such as Eurofer-97, where different kinds of microstructural inhomogeneities with sizes differing in order of magnitude may be simultaneously present.

Figure 2. Volume distribution in A. U. ($D(R)$ volume per unit volume of $Y_2O_3$ particles with a radius between $R$ and $R+dR$) for Eurofer ODS mechanically alloyed plus annealed at 750°C
Figure 3. Volume distribution in A. U. \((D/R)\)
volume per unit volume of \(Y_2O_3\) particles with a
radius between \(R\) and \(R+dR\) for Eurofer ODS
mechanically alloyed plus annealed at 1100°C, the
hatched area represents the 80% confidence band.

Figure 1 shows the nuclear SANS components of the as-milled powder and of the powders annealed at 750°C and 1100°C. The SANS spectrum of the mechanically alloyed powder serves only qualitatively as a reference and cannot be subtracted from the annealed ones. It is evident that, compared to the as-milled sample, small particles are present at 750°C. Their size slightly increases with increasing the temperature up to 1100°C. The corresponding size distributions, have been determined on a relative scale since the chemical composition of the scattering inhomogeneities is not precisely known and therefore the neutron “contrast” cannot be determined. These distributions, reported in figures 2 and 3 for 750°C and 1100°C annealing temperatures respectively, show a distribution of particles which are tentatively identified as Yttria ones. Furthermore, a growth of larger particles at 1100°C is observed, as also indicated by the small \(Q\) values of the corresponding SANS data, which might be attributed to nucleation of carbides. This is consistent with the observations made in [4]. It is evident that annealing at high temperature results in a redistribution of scattering centers sizes, but additional microstructural information and measurements extended to smaller \(Q\) values are needed to clarify these findings.

3. Conclusion - SANS is quite sensitive to microstructural changes produced under high temperature annealing in nano-structured Eurofer-97 ODS material, which turns out to be quite useful since these powders are difficult to observe by TEM. Micro-analytical information is needed to confirm the chemical composition of these scattering particles. Additional information is expected by planned high-resolution neutron diffraction measurements aiming to identify the crystallographic phases present in these powders. Once this experimental procedure will be fully developed it is planned to investigate by this technique the effect of annealing in a wider temperature range, including possibly \textit{in-situ} heating, in order to follow as closely as possible the onset and the evolution of the precipitate phases detected by these measurements.

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