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Investigation of microstructural evolution under neutron irradiation in Eurofer97 steel by means of small-angle neutron scattering

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ABSTRACT

Small-angle neutron scattering (SANS) has been utilized to investigate in Eurofer97 steel (9Cr, 0.01C, 1W, 0.2V Fe bal wt%) the microstructural effect of neutron irradiation at 300 °C up to a dose level of 8.4 dpa. For each irradiated sample an unirradiated reference was measured to distinguish as accurately as possible the actual effect of the neutron irradiation. The SANS measurements were carried out at the D22 diffractometer at the High-Flux Reactor of the Institut Max von Laue–Paul Langevin, Grenoble, France. Analysing separately the nuclear and magnetic SANS components obtained after subtraction of the reference from the irradiated sample it appears that the microstructural inhomogeneities produced under such irradiation conditions are non-magnetic ones, such as microvoids. Their size distributions are presented and compared with those previously obtained for the same steel irradiated at 2.5 dpa: with increasing the dose, the volume fraction is increased by a factor of 2 roughly, while the average size of these inhomogeneities remains nearly unchanged.

1. Introduction

This paper presents the results obtained by Small-Angle Neutron Scattering (SANS) measurements carried out to investigate the microstructural evolution in neutron irradiated Eurofer97. The SANS technique has already been successfully utilized in the microstructural investigation of Eurofer97 irradiated at the lower dose level of 2.5 dpa [1,2] as well as to characterize radiation effects in other fusion relevant raf/m steels such as F82H-mod. and Optifer [3–5]. SANS is extremely useful for such investigations because it allows to characterize defect distributions averaged in large sample volumes and to detect defect sizes smaller than the usual resolution limit of Transmission Electron Microscopy (TEM), that is approximately 10 Å; furthermore, the analysis of nuclear and magnetic SANS components provides a unique tool to check whether the defects produced under irradiation are magnetic ones or not, such as in the case of microvoids or helium bubbles. The neutron irradiated and reference Eurofer97 samples (9Cr, 1W, 0.2V, 0.1C wt%) were provided and prepared for the SANS measurements by FZK. They were irradiated at 300 °C at the HFR-Petten up to a target dose level of 8.4 dpa, in the frame of the SUMO-02 experiment [6,7]. Both the irradiated and the reference samples were approximately 1 cm^2 in surface and 1 mm thick. After recalling the experimental technique the results are presented and discussed with reference to the previous ones, obtained on the same steel irradiated at a lower dose level.

2. Experimental technique and data analysis

The SANS measurements were carried out at the D22 instrument at the High-Flux Reactor of the Institut Max von Laue – Paul Langevin, Grenoble. Sample-to-detector distances of 2.00 and 8.00 m with a wavelength, λ, of 6 Å were used. Defining the modulus of the scattering vector $Q = 4\pi \sin\theta/\lambda$ (where 2θ is the full scattering angle), these experimental conditions gave a Q interval ranging from 0.007 to 0.25 Å^{-1}, which corresponds to particle sizes ranging from 10 to 300 Å approximately. 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 [8]. 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 $d\Sigma(Q)/d\Omega$ (where Ω stands for the solid angle) can be written as the sum of two terms

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$$d\Sigma(Q)/d\Omega = d\Sigma(Q)/d\Omega_{\mathrm{nucl}} + d\Sigma(Q)/d\Omega_{\mathrm{mag}} \sin^2 \alpha, \tag{1}$$

where α is the azimutal angle on the detector plane. The ratio of the 'vertical' to the 'horizontal' SANS components:

$$R(Q) = \frac{d\Sigma(Q)/d\Omega_{nucl} + d\Sigma(Q)/d\Omega_{\mathrm{mag}}}{d\Sigma(Q)/d\Omega_{\mathrm{nucl}}} = 1 + (\Delta\rho)^2_{\mathrm{mag}}/(\Delta\rho)^2_{\mathrm{nucl}}, \tag{2}$$

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.

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

$$d\Sigma(Q)/d\Omega = (\Delta\rho)^2 \int_0^\infty dR\, N(R)\, V^2(R) |F(Q,R)|^2, \tag{3}$$

where $N(R)$ is the number per unit volume of centers with a typical size between R and $R + dR$; V, their volume and $|F(Q,R)|^2$ 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:

$$D(R) = N(R)R^3, \tag{4}$$

$N(R)$ was determined, by transformation of Eq. (3), using the method described by in [9] and more recently discussed in [10]. 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 Eurofer97, where different kinds of microstructural inhomogeneities with sizes differing in order of magnitude (e.g. fine microvoids and large precipitates) may be simultaneously present.

3. Results and discussion

Fig. 1(a) and (b) shows the nuclear SANS cross-section and $R(Q)$ ratio, respectively for Eurofer97 steel irradiated at 8.4 dpa and for its reference sample. The observed increase of the SANS cross-section for Q values around 10^{-1} Å^{-1} corresponds to the growth of defects 20–30 Å in size approximately. These defects are non-magnetic ones, since after the irradiation $R(Q)$ takes a nearly constant value of 2 approximately, which can be expected from Eq. (2) in the case of non-magnetic inhomogeneities imbedded in a fully magnetised martensitic matrix; therefore, they are tentatively identified as helium bubbles or microvoids, taking also into account the previous results obtained in this same steel irradiated at a lower dose level [2]. The $R(Q)$ values measured in the reference sample are correlated with the growth of carbide precipitates occurring in such steels after the standard metallurgical treatment [3–5]. For comparison with a lower dose level Fig. 2(a) and (b) shows the nuclear SANS cross-section and $R(Q)$ ratio respectively for Eurofer97 steel irradiated at 2.5 dpa and for its reference sample [2]: also in this case $R(Q)$ takes a value close to 2 after irradiation, suggesting the presence of helium bubbles or microvoids. In order to try and evaluate the actual effect of the neutron irradiation on Eurofer97 distinguishing it as accurately as possible from the effect produced under thermal annealing, the SANS cross-section of each reference samples has to be subtracted from the SANS cross-section of the corresponding irradiated sample [4,5]. Fig. 3(a) and (b) shows the nuclear SANS cross-section and $R(Q)$ ratio, respectively for the difference between irradiated and reference Eurofer97 at the two investigated dose levels of 2.5 and 8.4 dpa. In the investigated Q range, the SANS effect shown in

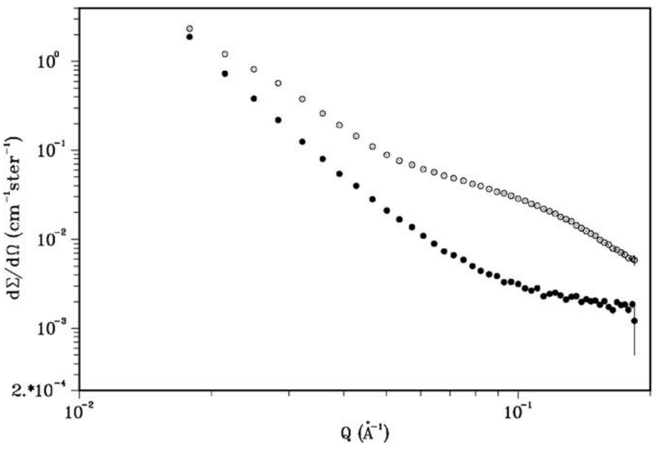

Fig. 1a. Nuclear SANS cross-sections of Eurofer97 steel neutron irradiated at 300 °C at 8.4 dpa (empty dots) and reference (full dots).

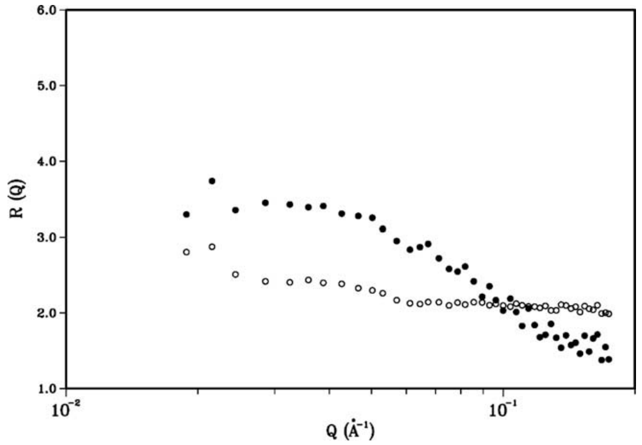

Fig. 1b. $R(Q)$ of Eurofer97 steel neutron irradiated at 300 °C at 8.4 dpa (empty dots) and reference (full dots).

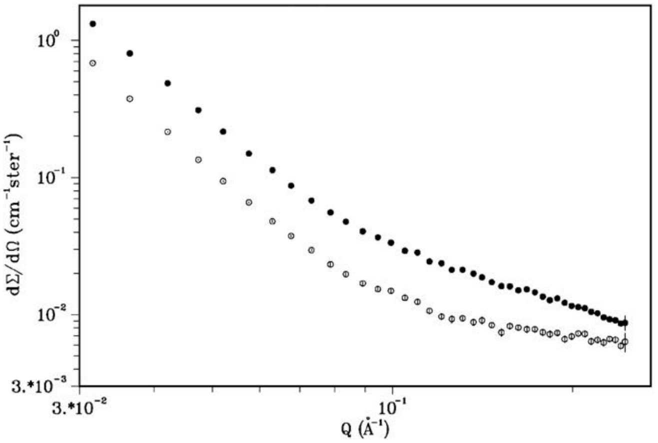

Fig. 2a. Nuclear SANS cross-section of Eurofer97 steel neutron irradiated at 300 °C at 2.5 dpa (full dots) and reference (empty dots) (after the results presented in Refs. [1,2]).

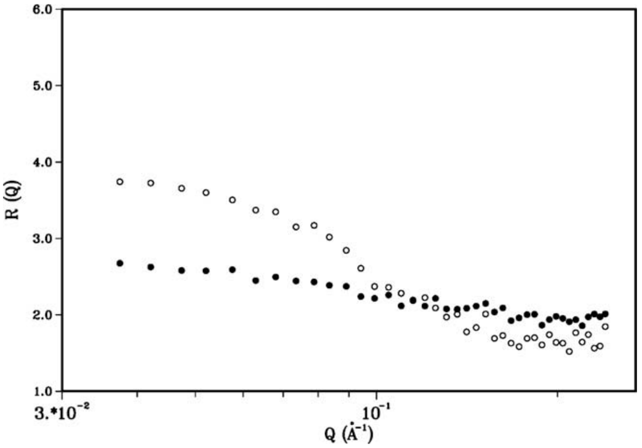

Fig. 2b. $R(Q)$ of Eurofer97 steel neutron irradiated at 300 °C at 2.5 dpa (full dots) and reference (empty dots) (after the results presented in Refs. [1,2]).

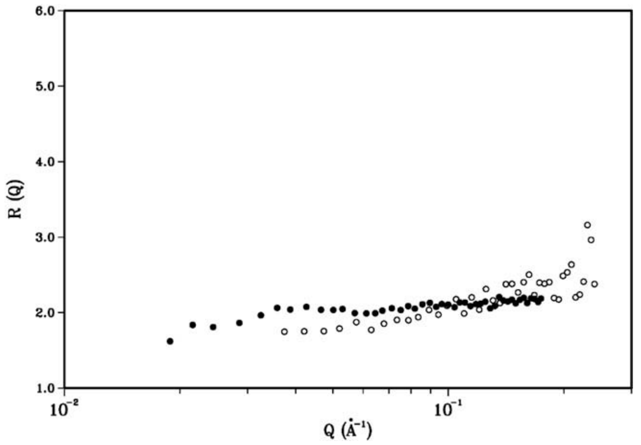

Fig. 3b. $R(Q)$ of the difference between Eurofer97 neutron irradiated at 300 °C at 2.5 dpa (full dots) and at 8.4 dpa (empty dots) and their respective reference samples.

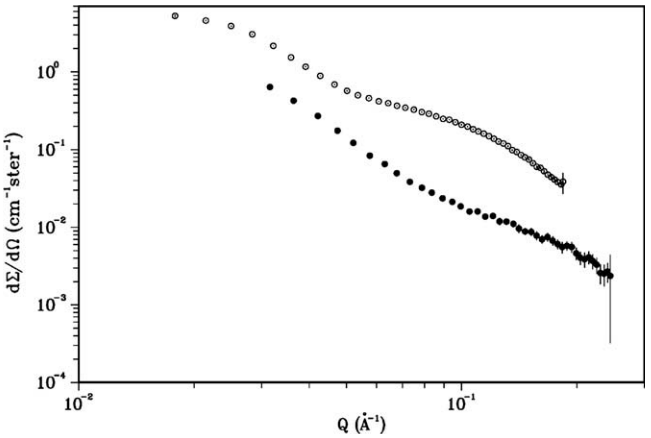

Fig. 3a. Nuclear SANS cross-sections of the difference between Eurofer97 neutron irradiated at 300 °C at 2.5 dpa (full dots) and at 8.4 dpa (empty dots) and their respective reference samples.

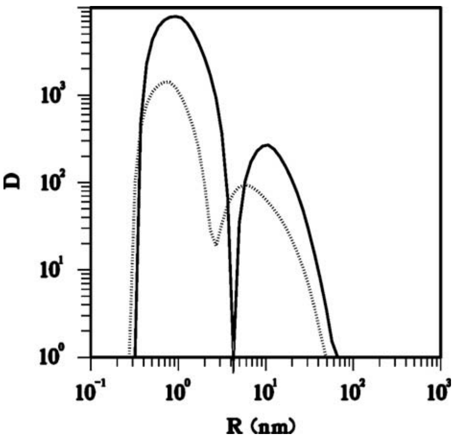

Fig. 4. Volume distribution functions $D(R)$ (nm^{-1}) obtained from the nuclear SANS difference between Eurofer97 neutron irradiated at 300 °C and their respective reference samples: 2.5 dpa dotted line, 8.4 dpa continuous line.

Fig. 3(a) is consistently higher at higher dose, implying a corresponding increase in the volume fraction; within the experimental uncertainties $R(Q)$ is close to 2 for both spectra. Both helium bubbles and microvoids are expected to behave as non-magnetic holes in the fully magnetised matrix of the Eurofer97 steel and are consequently hardly distinguishable by SANS. Also non-magnetic carbide precipitates, such as those observed in other ferritic/martensitic steels under irradiation [11], would behave as non-magnetic holes giving rise to a similar SANS effect, but for such irradiation conditions microvoids and helium bubbles are the most frequently observed microstructural defects in Eurofer97. Furthermore, given the very low B content of this steel the occurrence of equilibrium bubbles filled with helium seems unlikely because there might not be enough helium to fill and stabilize the vacancy clusters [12]; the presence of microvoids around large precipitates is also confirmed by TEM observations [12] on this material irradiated under similar conditions. A preliminary analysis of the SANS spectra shown in Fig. 3(a) has therefore been carried out assuming that the defects produced under the investigated irradiation conditions are microvoids and taking, therefore, the neutron 'contrast' simply as the neutron scattering length density of the Eurofer steel, that is $(\Delta\rho)^2 = 5.70 \times 10^{-19}$ cm^{-4} [13]; in case, such inhomogeneities were helium bubbles, a more complex data analysis would be required taking into account the dependence of the bubble radius on the helium pressure inside the bubble itself [14,15]. The obtained volume distributions are presented in Fig. 4: increasing the dose the average radius remains nearly unchanged but a consistent increase is observed in the volume fraction, determined as 0.005 at 2.5 dpa and as 0.011 at 8.4 dpa. The uncertainty on these distributions and on the corresponding metallurgical parameters is approximately 20%.

4. Conclusions

The SANS investigation of the microstructural effect of neutron irradiation on Eurofer97 steel shows that at 300 °C increasing the irradiation dose from 2.5 dpa to 8.4 dpa non-magnetic defects grow increasing in volume fraction by a factor of 2, while their average size remains nearly unchanged. This effect refers to defects in the range 20–30 Å. The comparison of nuclear and magnetic SANS shows that such defects are non-magnetic ones and preliminary TEM results suggest that they can tentatively be identified as microvoids. However, systematic TEM observations are necessary to confirm this and to check whether the smaller defects, around 10 Å in size, and the larger ones shown in Fig. 4 have the same composition. These results seem in any case to confirm the good resistance of the Eurofer97 steel to the microstructural effect of neutron irradiation at 300 °C up to 8.4 dpa.

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