

# Microstructural investigation of low-dose neutron irradiation effects in martensitic steels for nuclear application by means of small-angle neutron scattering

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The microstructural effect of low-dose neutron irradiation and subsequent high-temperature tempering in the reduced activation ferritic/martensitic steel F82H-mod. (7.73 Cr, 0.09 C, 0.08 Mn, 0.19 V, 2.06 W, 0.02 Ta, wt%, bal. Fe) has been studied using small-angle neutron scattering (SANS). The investigated samples were irradiated with thermal neutrons at 523 K, to dose levels of 2.4 displacements per atom then tempered for 2 h at 1043 K. The SANS measurements were carried out at the D22 instrument of the High Flux Reactor at the Institut Max von Laue–Paul Langevin, Grenoble, France. The differences observed in nuclear and magnetic small-angle neutron scattering cross-sections after subtraction of the reference sample from the irradiated one suggest that the irradiation and the subsequent post-irradiation tempering produce the growth of non-magnetic precipitates; the results are also compared with those obtained on other ferritic/martensitic steels, with different chemical composition, irradiated under the same conditions.

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## 1. Introduction and material characterization

Under neutron irradiation, complex microstructural phenomena occur in ferritic/martensitic steels for future fusion reactors and for accelerator driven systems, implying changes in precipitate composition and the growth of helium bubbles and microvoids, with consequent changes in the thermo-mechanical properties (Hishinuma *et al.*, 1998). These phenomena require careful experimental investigation to identify and characterize the different kinds of defects. Transmission electron microscopy (TEM) observations, although indispensable, are limited for statistics and because of the defocusing effects produced by the magnetic matrix. Small-angle neutron scattering (SANS), coupled with TEM, is therefore quite useful for such investigations. In fact, as it is also shown by previous works (Coppola, Klimiankou *et al.*, 2004; Coppola *et al.*, 2005; 2006; 2007), SANS measurements provide an additional tool to try and distinguish non-magnetic defects, such as microvoids or helium bubbles, and magnetic ones, such as certain kinds of precipitates produced under irradiation for different dose levels in steels differing for their initial chemical compositions. This contribution presents new results of a SANS study carried out to investigate the microstructural effect of neutron irradiation and subsequent tempering in the reduced activation ferritic/martensitic steel F82H-mod. (7.73 Cr, 0.09 C, 0.08 Mn, 0.19 V, 2.06 W, 0.02 Ta, Fe bal. wt%), developed in view of its possible use in fusion reactors (Schirra, 1995) and previously investigated by SANS to study precipitation phenomena (Coppola, Ehrlich *et al.*, 1998) and the growth of helium bubbles under  $\alpha$ -particle implantation (Coppola *et al.*, 2000; Coppola, Klimiankou *et al.*, 2004). For comparison, previous

results (Coppola *et al.*, 2007) obtained under the same irradiation conditions on a similar ferritic/martensitic steel, the Optifer steel (9.3 Cr, 0.1 C, 0.50 Mn, 0.26 V, 0.96 W, 0.066 Ta Fe bal. wt%) (Ehrlich *et al.*, 1994) are quoted.

The chemical composition of ferritic/martensitic steels such as F82H-mod. or Optifer is defined in order to replace elements such as Ni or Nb, having a high activation rate under neutron irradiation, with more favourable ones such as W or Ta (Hishinuma *et al.*, 1998). That implies a better resistance to irradiation and a lower activation under the expected service conditions, but from the metallurgical point of view the precipitation behaviour is substantially different with respect to conventional ferritic/martensitic steels. Both the F82H-mod. and the Optifer samples were irradiated by exposure to thermal neutrons at the High Flux Reactor–Petten (The Netherlands), up to dose levels of 2.4 dpa (displacement per atom) at 523 K. Some of these samples underwent tempering treatments of 2 h at 1043 K after the irradiation. Unirradiated reference samples, submitted to the same thermal treatments as the irradiated ones, were also prepared. The size of both the irradiated and unirradiated specimens utilized for the SANS experiments was 4 x 10 mm<sup>2</sup> in surface and 1 mm in thickness.

The results of TEM observations of these F82H-mod. samples (Materna-Morris *et al.*, 1999) show that after irradiation precipitates such as (Fe, Cr, V, W)<sub>23</sub>C<sub>6</sub>, WC or TaC, are present, together with a very low volume fraction of microvoids and helium bubbles compared with similar steels, such as Optifer, irradiated under the same conditions. However it is difficult to obtain quantitative information from such local observations, which are limited both in

statistics and because of the TEM resolution in such magnetic materials.

## 2. Experimental technique

Reference is made to Kistorz (1996) and Hutchings & Windsor (1987) for a general presentation of SANS and to our previous works (Coppola *et al.*, 2000; Coppola, Dewhurst *et al.*, 2004; Coppola, Klimiankou *et al.*, 2004) for its application to the study of martensitic steels. SANS measurements were carried out using the D22 diffractometer at the Institut Max von Laue–Paul Langevin (ILL), in Grenoble. The experimental conditions were a neutron wavelength  $\lambda$  of 6 Å and a sample-to-detector distance of 2 m. Defining the scattering vector  $Q = 4\pi\sin\theta/\lambda$ , where  $2\theta$  is the scattering angle and  $\lambda$  the neutron wavelength,  $Q$  values ranging between 0.03 Å<sup>-1</sup> and 0.2 Å<sup>-1</sup> were obtained, corresponding in the real space to particle sizes ranging between approximately 10 and 100 Å. After correction for background noise, detector efficiency and attenuation factor, the value of the SANS cross-section in physical units (cm<sup>-2</sup> sterad<sup>-1</sup>) was obtained by a calibration of the neutron flux, measuring water in a quartz cell, and by means of the ILL standard programs (Ghosh *et al.*, 1998). The SANS cross-section of the reference samples was subtracted from the SANS cross-section of the corresponding irradiated samples in order to distinguish, as accurately as possible, the effect of the irradiation itself from all the other microstructural effects arising during the heating at 523 K for a duration corresponding to the irradiation time.

In the case of magnetic samples, the total SANS cross-section  $d\Sigma(Q)/d\Omega$  (where  $\Omega$  stands for the solid angle) can be written as:

$$d\Sigma(Q)/d\Omega = d\Sigma(Q)/d\Omega_{\text{nuc}} + d\Sigma(Q)/d\Omega_{\text{mag}} \sin^2\alpha, \quad (1)$$

where  $d\Sigma(Q)/d\Omega_{\text{nuc}}$  and  $d\Sigma(Q)/d\Omega_{\text{mag}}$  are the nuclear and magnetic SANS cross-sections, respectively, and  $\alpha$  is the azimuthal angle on the detector plane.

In the present case a saturating horizontal magnetic field of 1 T was applied perpendicular to the incoming neutron beam in order to distinguish  $d\Sigma(Q)/d\Omega_{\text{nuc}}$  and  $d\Sigma(Q)/d\Omega_{\text{mag}}$  in such a way that 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).

The nuclear plus magnetic to nuclear cross sections ratio can be written as:

$$R(Q) = [d\Sigma(Q)/d\Omega_{\text{nuc}} + d\Sigma(Q)/d\Omega_{\text{mag}}]/d\Sigma(Q)/d\Omega_{\text{nuc}} \\ = 1 + (\delta\rho)_{\text{m}}^2/(\delta\rho)_{\text{n}}^2, \quad (2)$$

where  $(\delta\rho)_{\text{m}}^2$  and  $(\delta\rho)_{\text{n}}^2$  are, respectively, the neutron magnetic and nuclear scattering length density square differences between matrix and the microstructural inhomogeneities giving rise to the observed SANS effect (Kistorz, 1996; Hutchings & Windsor, 1987). In complex steels, such as the one investigated in this study, inhomogeneities with different chemical composition and size are generally present after irradiation, reflecting a more or less marked dependence on  $Q$  of the  $R(Q)$  ratio; if  $R(Q)$  is constant in  $Q$  a homogeneous defect composition can be assumed. Previous studies on unirradiated and irradiated ferritic/martensitic steels (Coppola, Kampmann *et al.*, 1998; Coppola *et al.*, 2005, 2007) have shown that the measured  $R(Q)$  values can be correlated with the different inhomogeneities present in the investigated material. However the chemical compositions of such inhomogeneities, especially in the case when they are precipitates, must be determined by other techniques, such as TEM, in order to

unambiguously identify them from the measured  $R(Q)$  values and to fully exploit the metallurgical information obtainable by such measurements (Coppola, Kampmann *et al.*, 1998; Coppola, Dewhurst *et al.*, 2004).

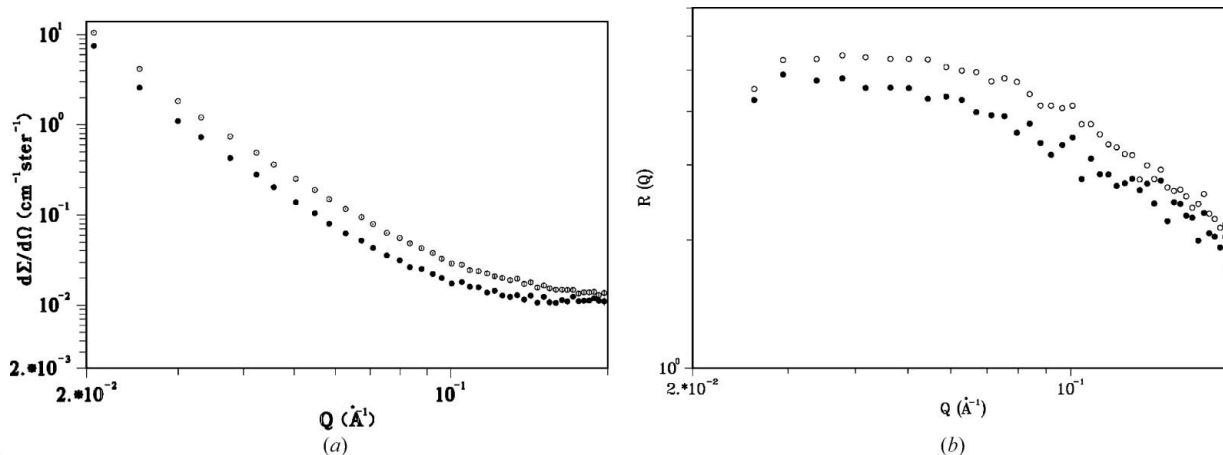
The size distributions were determined by indirect transformation of the SANS cross-section:

$$d\Sigma(Q)/d\Omega = (\delta\rho)^2 \int_0^\infty dR N(R) V^2(R) |F(Q, R)|^2, \quad (3)$$

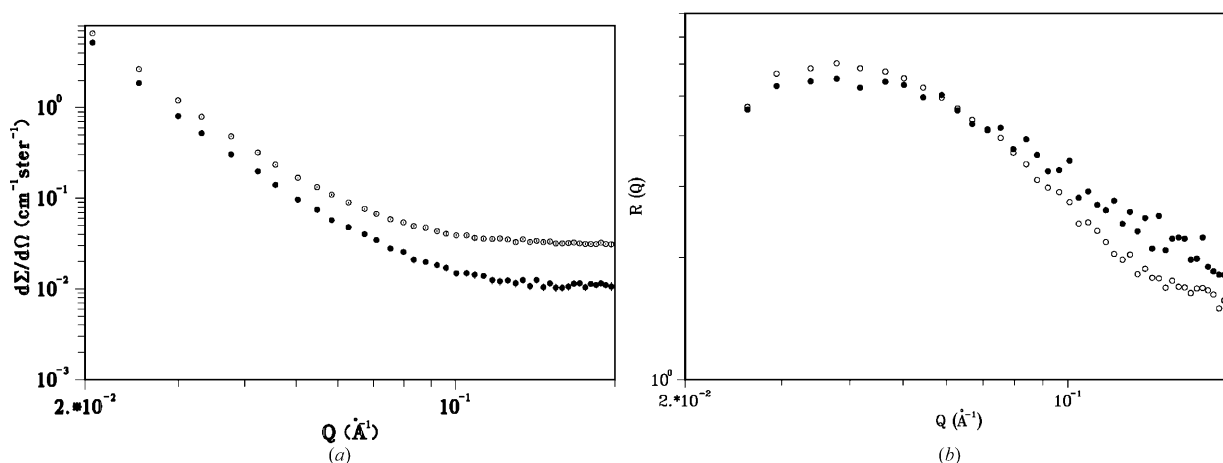
where  $N(R)$  is the number per unit volume of centres with a typical size between  $R$  and  $R + dR$  [the volume distribution function is  $D(R) = N(R)R^3$ ],  $V$  their volume and  $|F(Q, R)|^2$  their form factor (assumed spherical in this case) and  $(\delta\rho)^2$  is the ‘contrast’ or square difference in neutron scattering length density between the scattering inhomogeneities and the metallic matrix (Hutchings & Windsor, 1987). Equation (3) was solved using the method reported in (Magnani *et al.*, 1988) and more recently discussed in (Coppola, Kampmann *et al.*, 1998). For the reasons discussed in these two papers the quality of the best-fit is optimized by choosing an interval in  $R$  as large as possible, namely varying between 4 and 400 Å in the present case; however the uncertainty band associated to the distribution functions for  $R < 10$  Å is quite large (50% or even more), reflecting the fact that this value is close to the resolution limit of the SANS technique and that no quantitative information can safely be obtained for such small sizes. It is emphasized that since the microstructural inhomogeneities giving rise to the SANS effects measured in the investigated samples are only tentatively identified in this case, the size distributions presented in the next section have not to be considered as conclusive ones from a metallurgical point of view but simply as an additional tool in the analysis and discussion of the SANS data.

## 3. Results and discussion

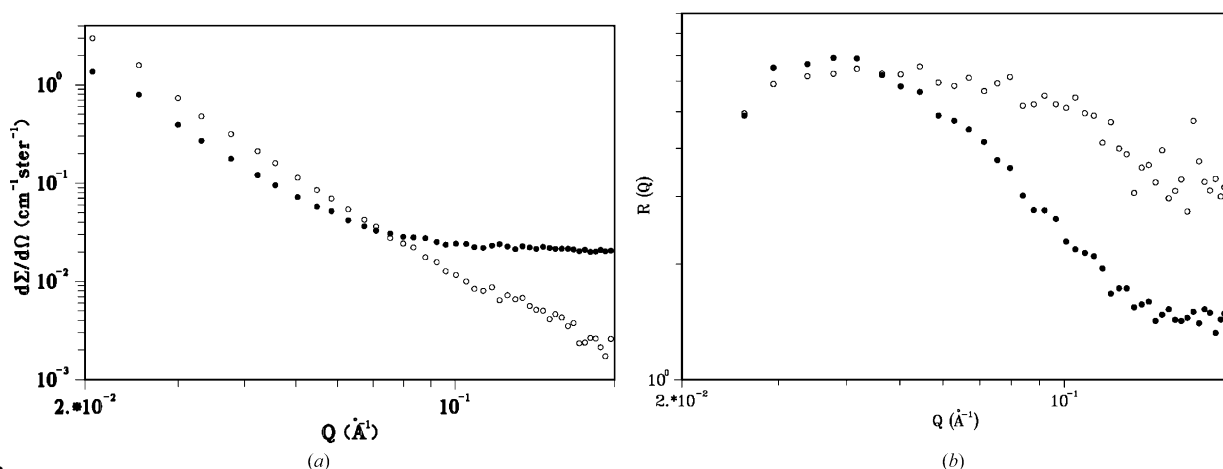
After irradiation to 2.4 dpa a consistent increase in the SANS cross-sections of the irradiated F82H-mod. sample with respect to the reference one is observed (Fig. 1*a*), indicating a high density of irradiation defects in a size range extending to 100 Å approximately. Fig. 1*b*) shows that for these same two samples the corresponding  $R(Q)$  ratio is substantially unchanged after irradiation and takes values corresponding to those detected in the unirradiated material after tempering at 823 K, where the precipitation of the (Fe, W)C phase is expected (Coppola, Ehrlich *et al.*, 1998). It is also evident that the microstructural defects produced under irradiation don’t have a homogeneous chemical composition. Tempering 2 h at 1043 K after the irradiation produces a similar effect in the SANS cross-sections and  $R(Q)$  ratios of the irradiated sample with respect to the reference one (Fig. 2). Figs. 3*a*) and *b*) show the nuclear SANS cross-section and the  $R(Q)$  ratio obtained for the difference between the irradiated and the reference sample, both in the as-irradiated condition and after the post-irradiation tempering. It is evident that the actual effect of the irradiation is quite different in the two cases. In fact, just after the irradiation a population of defects as large as 100 Å in average size is detected; the measured  $R(Q)$  ratio is nearly constant over most of the investigated  $Q$  range with a value close to the one detected for tempering at 823 K in the unirradiated material. After tempering the SANS cross-section is completely modified by the appearance of a flat background, corresponding to a strong increase in the population of defects having a size below 10 Å; also the  $R(Q)$  value is drastically



**Figure 1** F82H-mod. steel samples irradiated with 2.4 dpa at 523 K (empty dots) and reference (full dots). (a) Nuclear SANS cross section and (b)  $R(Q)$ .



**Figure 2** F82H-mod. steel samples irradiated with 2.4 dpa at 523 K then tempered 2 h at 1043 K (empty dots) and reference (full dots). (a) Nuclear SANS cross-section and (b)  $R(Q)$ .

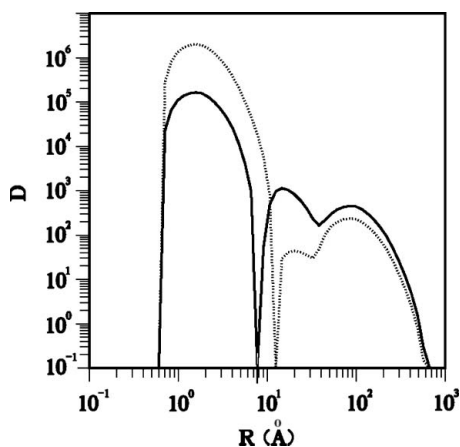


**Figure 3** Difference between irradiated (empty dots irradiated with 2.4 dpa at 523 K, full dots irradiated with 2.4 dpa at 523 K then tempered 2 h at 1043 K) and reference F82H-mod. samples. (a) Nuclear SANS cross section and (b)  $R(Q)$ .

changed showing a much stronger dependence on  $Q$  and much smaller value for high  $Q$ 's.

Fig. 4 shows the size distributions obtained from the SANS data of Fig. 3(a), where the growth of very small defects after tempering is clearly visible. Assuming that by subtracting the reference sample from the irradiated one the actual effect of the irradiation itself in the material is correctly estimated and based on what is known on the

microstructural evolution of the F82H-mod. steel from previous studies (Coppola, Ehrlich *et al.*, 1998) the results shown in Fig. 3 can tentatively be interpreted by attributing the SANS effect in the as-irradiated material to the precipitation of the (Fe, W)C phase; tempering at 1043 K would dissolve it, promoting the growth of very small nuclei of a new phase, possibly (Cr, Fe)<sub>23</sub>C<sub>6</sub> carbides, as it is suggested by the corresponding  $R(Q)$  values (Coppola, Ehrlich *et al.*,

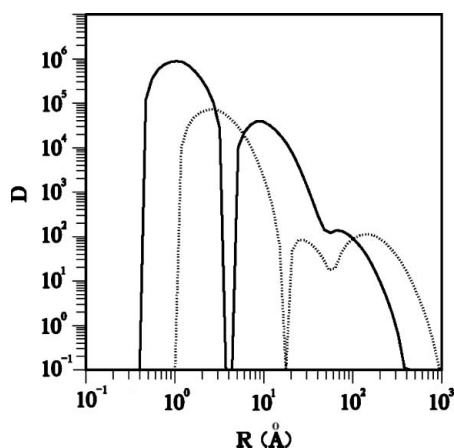


**Figure 4**

Volume distribution function  $d(R)$  (in arbitrary units) vs defect radius  $R$  (Å) for F82H-mod. steel irradiated with 2.4 dpa at 523 K (continuous line) and irradiated with 2.4 dpa at 523 K then tempered 2 h at 1043 K (dotted line); the experimental error bands of such distributions, not reported in the picture, are 20% approximately. These distributions are obtained by transformation of the nuclear component of the difference between each irradiated sample and its reference.

1998). Although no conclusive metallurgical interpretation is possible based on these data, this would be qualitatively consistent with what is already known on the precipitation behaviour of the unirradiated material and with the fact that only a very low volume fraction of helium bubbles and microvoids could be detected by TEM in this steel compared with similar ones (Materna-Morris *et al.*, 1999).

As a matter of fact, in the case of the Optifer steel quite different SANS results have been obtained (Coppola *et al.*, 2007). In the investigated  $Q$  range, the SANS effect after subtraction of the reference sample is much higher before tempering at 1043 K and  $R(Q)$  takes a nearly constant value of approximately 2, which has to be expected from equation (2) in the case of non-magnetic inhomogeneities embedded in a fully magnetized martensitic matrix. Such inhomogeneities were tentatively identified as helium bubbles or, more likely, microvoids given the very low helium concentration expected under these irradiation conditions in this steel (Materna-



**Figure 5**

Volume distribution function  $d(R)$  (in arbitrary units) vs defect radius  $R$  (Å) for Optifer irradiated with 2.4 dpa at 523 K (continuous line) and irradiated with 2.4 dpa at 523 K then tempered 2 h at 1043 K (dotted line); the experimental error bands of such distributions, not reported in the picture, are 20% approximately [after the work of Coppola *et al.* (2007)]. These distributions are obtained by transformation of the nuclear component of the difference between each irradiated sample and its reference.

Morris *et al.*, 1999). The growth of these non-magnetic defects following post-irradiation treatment was shown also by a preliminary analysis of the size distributions of irradiated sample. It can be seen in Fig. 5 that the volume fraction of defects as small as 10 Å [with a corresponding  $R(Q)$  value close to 2] is almost one order of magnitude larger in the as-irradiated sample, while defects one order of magnitude larger grow during post-irradiation tempering.

#### 4. Conclusions

In the reduced activation F82H-mod. steel, neutron irradiated at 523 K with 2.4 dpa, a high density of inhomogeneities as large as 100 Å is detected; a subsequent tempering at 1043 K appears to dissolve these inhomogeneities and to promote the growth of a new phase with sizes one order of magnitude smaller. Since these results refer to the difference in the SANS cross-sections of the irradiated and the reference samples, the observed SANS effect should not be attributed to defects arising from the thermal treatment but to the actual microstructural radiation damage; based also on previous results on the unirradiated F82H-mod. steel the observed SANS effect is tentatively attributed to the growth of the (Fe, W)C phase under irradiation, followed under tempering by its dissolution into nuclei of a new phase (possibly carbide precipitates). In the Optifer steel under the same irradiation conditions the SANS effects are tentatively correlated with the occurrence of microvoids under irradiation, growing to sizes one order of magnitude larger under a subsequent tempering at 1043 K. This interpretation of the SANS effects observed in the two investigated steels, which correlates with what is currently known from TEM observations and basic metallurgical knowledge, would imply for the F82H-mod. steel a better resistance to microcavitation under low-dose irradiation but a higher phase instability.

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