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Small-angle neutron scattering study of the nano-sized features in an oxide dispersion strengthened Fe12Cr alloy

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Abstract

Small-angle neutron scattering experiments, along with positron lifetime measurements and transmission electron microscopy observations, were performed on samples of an oxide dispersion strengthened Fe12Cr alloy, and its non-oxide dispersion strengthened counterpart, in order to characterize their nano-sized features. The nuclear and magnetic scattering data were analysed using the maximum entropy approach for obtaining the size distribution of the scattering centres in these materials. The positron annihilation results and the transmission electron microscopy information have made possible an interpretation of the volume distribution of the scattering centres having sizes below ~ 16 nm and their proper quantitative analyses. The smaller scattering centres in the oxide dispersion strengthened alloy exhibit distributions with modal values at ~ 6-7 and 12-14 nm. The peak at ~ 6-7 nm appears to be due to overlapping of more than one type of scattering centres while the one at ~ 12 -14 nm can be exclusively attributed to Y-rich centres. The quantitative analysis of the magnetic scattering data yields a volume fraction and number density of Y-rich particles estimated in $0.70\pm0.03\%$ and $0.77\times10^{22} \text{ m}^{-3}$, respectively.

Keywords: oxide dispersion strengthening; small-angle neutron scattering; maximum entropy method; positron annihilation spectroscopy; transmission electron microscopy

1. Introduction

The development of advanced structural materials, such as oxide dispersion strengthened (ODS) alloys, is mandatory for building efficient and safe fusion and generation IV fission reactors. Thus, it is of top priority to understand the characteristics of the particle dispersion responsible for the enhanced mechanical behaviour and radiation resistance that exhibit ODS alloys. Advanced analytical and high-resolution transmission electron microscopy (TEM) methods and atom probe tomography (APT) are the techniques that contribute most significantly to get insight into the composition, size and structure of nano-sized particles, or atom clusters, dispersed in ODS materials [1–5]. Small angle neutron scattering (SANS) is also a technique used recurrently to evidence the presence of a nano-sized dispersion in these alloys, and to achieve information on the sizes of the dispersoids [6–11]. SANS, compared with TEM and APT, can give a more useful information on the size distribution of nano-sized features in a matrix since it samples a macroscopic volume. Nevertheless, the success of SANS for studying a dispersion of nano-particles in ODS steels is relatively limited because it cannot provide a direct information on the dispersoid composition and requires certain assumptions concerning the chemical composition and morphology of the dispersoids. Also, it is frequent to assume log-normal or Gaussian functions for describing the size distribution of different scattering centre populations. Consequently, the results are biased by the starting assumptions applied to the data analysis. This is particularly critical when several dispersed phases coexist in the matrix, and moreover, the corresponding size distributions might be overlapped. This is the case for ODS steels. The interpretation of SANS measurements has been usually made applying the Guinier and Porod approximations, or the unified model approach, to the scattering curve obtained directly from the material sample, or after subtracting the scattering data obtained from a reference sample that is

free of the dispersion investigated [6–11]. However, this subtraction approach appears not to be a suitable procedure because the reference non-ODS material, although free of the specific dispersoids, may very likely contain other secondary phase particles as a result of its particular processing route, which may be different from the ones for the ODS material. In contrast, the maximum entropy approach for analysing the SANS data does not require any previous assumption on the type and number of size distribution functions to be fitted allowing to reveal complex situations that could arise from overlapping distributions without applying any bias [12].

Herein, the results from SANS experiments performed on an ODS Fe-Cr model alloy, analysed using the maximum entropy method, are reported along with the corresponding ones for the counterpart non-ODS alloy. The results allow discriminate more realistically the features attributable to the nano-sized Y-rich particles from the ones corresponding to other nano-sized features also present in these alloys as TEM analyses have revealed [2, 13].

2. Experimental

The ODS alloy with nominal composition Fe-12%Cr-0.4%Y₂O₃ (wt %), and the counterpart non-ODS alloy, i.e. Fe-12%Cr, were produced by mechanical alloying and hot isostatic pressing (HIP) following the procedure described elsewhere [2, 14]. The Fe and Cr elemental powders were milled in Ar atmosphere for 15 h. For the ODS alloy, further milling for 12 h under the same conditions was carried out to disperse the Y₂O₃ powders. The C contents measured by IR absorption in the alloys were (0.41±0.09) at% and (0.32±0.07) at% in the ODS Fe12Cr and Fe12Cr alloys, respectively.

Comprehensive TEM and APT studies of these alloys in the as-HIP condition and heat treated at 1023 K have been previously reported [2]. For the as-HIP alloys, Cr oxides and Fe_xC carbides are present, as well as a dispersion of Y-rich particles in the case of the ODS alloy. Annealing induces transformation of the metastable carbides into larger M_{23}C_6 (M=Cr, Fe) carbides. In addition, small nanovoids (< 5 nm) are observed before and after annealing in the ODS alloy [2, 13, 14].

The SANS measurements were carried out in the FRM II research reactor at Garching (Germany) using the KWS-2 diffractometer with a neutron wavelength of 7 Å and sample-detector distances of 2, 8 and 20 m. The measurements were performed with a magnetic field of 1.4 T applied normal to the incident beam. In this way, the magnetic moments of the magnetic atoms are aligned with the applied saturating magnetic field. The scattered intensities from the alloys were corrected subtracting background counts and taking into account the detector efficiency. The instrumental resolution effects on the scattering curves were also taken into account using a suitable resolution function of the diffractometer. The scattered intensities were calibrated in absolute units using a Plexiglass sample as secondary reference standard to obtain the integrated scattering cross section value $\Delta\Sigma/\Delta\Omega$ from the scattering centres embedded in the matrix. The scattering centres in these alloys would be particles having different composition, structure and sizes, i.e. carbides, small oxides particles, or solute nano-clusters, and some other structural defects inherent to the alloy processing. Thus, the changes in the scattering curves, induced by the alloy composition or the thermal treatment, can be explained in terms of variations in the fraction, composition and size distribution of the secondary phase particles and defects. The scattering data were analysed applying the two phase model consisting in a homogeneous matrix with one type of polydispersed particles

[15]. In this approach the scattered intensity, i.e. the differential scattering cross section per volume unit, $I(Q)$ (cm^{-1}), as a function of the scattering vector Q is given by

$$I(Q) = (\Delta\eta)^2 \int n(R) [V(R)]^2 [F(Q, R)]^2 dR \quad (1)$$

where $\Delta\eta$ is the scattering contrast, $n(R)$ the number density of scattering centres with a radius between R and $R+dR$, and $V(R)$ and $F(Q, R)$ the volume and the form factor of the scattering centres. $\Delta\eta$ is given by the difference between the scattering length density for the centre η^c and the matrix η^m . In the case of a ferromagnetic matrix as Fe12Cr, in addition to the nuclear scattering due to differences in the composition and structure between the scattering centres and the matrix, magnetic scattering could exist when the difference between the resultant magnetic moment of the centres and the magnetised matrix is high enough. Now, the scattered intensity is controlled by the magnetic scattering contrast $\Delta\eta_{\text{mag}} = (\eta_{\text{mag}}^c - \eta_{\text{mag}}^m)$. When the centres are not magnetic, they can be considered magnetic holes in a ferromagnetic matrix and the magnetic scattering contrast would be $\Delta\eta_{\text{mag}} = \eta_{\text{mag}}^m$. Then, when the sample is magnetised with a strong applied field normal to the incident beam, the scattered intensity results to be

$$I(Q, \phi) = I_{\text{nuc}}(Q) + I_{\text{mag}}(Q) \sin^2 \phi \quad (2)$$

where ϕ is the angle between the applied field and the scattering vector. The magnetic contribution is due to the component of the magnetic moments of the atoms perpendicular to the scattering vector Q . For $\phi=0$, the magnetic contribution to the scattered intensity is zero and $I(Q, 0) = I_{\text{nuc}}$. Therefore, the contribution of the magnetic scattering to the intensity can be obtained from the difference between the intensity measured at $\phi=\pi/2$ and that one measured at $\phi=0$.

In the case of a two-phase system, the so-called A ratio given by the ratio of the values of $I(Q, \pi/2)$ to $I(Q, 0)$ is related with the nuclear and magnetic contrasts of the scattering centres by [16]

$$A(Q) = \frac{I(Q, \pi/2)}{I(Q, 0)} = 1 + \frac{(\Delta\eta_{mag})^2}{(\Delta\eta_{nuc})^2} \quad (3)$$

Then, a Q independent A ratio through a given range of Q values indicates scattering centres with a constant composition for the corresponding size range. In this case, if the centres are non-magnetic $\Delta\eta_{mag} = \eta_{mag}^m$, and information on the composition of the centres can be achieved via the $\Delta\eta_{nuc} = (\eta_{nuc}^c - \eta_{nuc}^m)$ value.

The SANS data were analysed with the Irena 2.50 SAS macro package for Igor Pro [17], using the MaxEnt algorithm developed in Ref. [18].

In addition, TEM observations and positron annihilation lifetime spectroscopy (PALS) measurements were performed on samples of these alloys for identifying the nature of the nano-sized features. The TEM observations were carried out in a Philips CM20 microscope operated at 200 kV and equipped with an X-ray energy dispersive spectrometer. A ^{22}Na positron source sealed inside thin kapton foils and sandwiched between a pair of identical samples was used for the positron annihilation measurements. The experiments were accomplished using a conventional fast-fast coincidence spectrometer with time resolution system of 230 ps (FWHM). The lifetime spectra were collected up to acquire a count total $> 10^6$. The instrumental time resolution and source correction terms were obtained from a reference spectrum of annealed iron. The positron annihilation lifetime spectra were analysed in terms of one or two lifetime components, τ_1 and τ_2 , and the mean positron lifetime defined by

$$\langle \tau \rangle = \tau_1 I_1 + \tau_2 I_2 \quad (4)$$

where I_1 , and I_2 are the corresponding intensities for each component.

3. Results and discussion

Figure 1 shows the maximum entropy fits to the nuclear and magnetic scattering data. The simple comparison of the curves reveals the presence of a higher number of nano-sized features in the ODS alloy after heating at 1023 K. The volume distributions of the centres obtained from the fits are depicted in Figures 2 and 3.

3.1. *Volume distributions of particles*

The volume distribution obtained from the nuclear scattering data for the ODS Fe12Cr alloy, see Figure 2, shows two nano-sized features with modal values at ~ 6, and 13 nm that are relatively insensitive to the heat treatment, at first glance. The Fe12Cr alloy in the as-HIP condition also exhibits two nano-sized features with modal values at ~ 7, and 14 nm, which were remarkably altered by the heat treatment at 1023 K as Figure 2 shows. The distribution with modal value at ~ 14 nm disappeared and the number of remaining nano-sized centres decreased shifting the mode at ~ 6 nm. The behaviour of the larger size features is comparable to that observed for the ODS Fe12Cr alloy.

The distinctive behaviour of the bimodal distribution in the ODS Fe12Cr alloy would have to be attributed to the presence of Y-rich nanoparticles, in agreement with the APT and TEM results reporting mean sizes values of 9 ± 6 nm in samples of this same material [2]. Nevertheless, as some other nano-sized centres remain in the counterpart non-ODS alloy after the heat treatment, this would indicate that the corresponding modal peak at ~

7 nm in the ODS Fe12Cr alloy may not be exclusively attributed to features associated with Y, that is, this modal peak could be an overlapped distribution of different nano-sized scattering centres. The same is suggested by the behaviour of the modal peak at ~14 nm in the Fe12Cr alloy, which disappears completely after the heat treatment meanwhile the counterpart in ODS Fe12Cr alloy remains. This also occurs for the corresponding modal peaks found in the distributions obtained from the magnetic scattering data, see Figure 3. The origin of these modal peaks will be discussed in section 3.3.

In addition, larger size features with diameters $D > 16$ nm are found for both alloys in the as-HIP condition. After the heat treatment the features in the size range 16 – 40 nm disappeared and the population of centres with sizes above 65 nm increased, see Figure 2. The heat treatment effect on the size distribution of the larger features reflects the transformation of the small metastable Fe_xC carbides into M_{23}C_6 and subsequent coarsening, already observed by TEM in samples of these alloys. For either alloys in the as-HIP condition, the major part of the centres with sizes $D > 45$ nm is expected to be Cr-rich oxides, Cr_2O_3 mainly, as revealed by TEM and APT analyses. The increase of the number of centres with sizes above ~ 80 nm induced by the heat treatment may be attributed to overlapping of the M_{23}C_6 particle distribution with the one corresponding to Cr-oxide particles, according with previous TEM and APT analyses [2]. Since the respective morphologies and chemical compositions for the oxide and carbide particles appear to be variable, i.e. a unique composition for each type of these particles could not be determined from the TEM and APT analyses, and moreover the size distributions appear to be overlapped, a quantitative analysis of the volume distribution of the these particles cannot be accomplished. Thus, the following results and discussion will be focused on the features with $D < 16$ nm, which is actually the size range of concern for a strengthener dispersion.

The analyses of the magnetic scattering data result in volume distributions for the nano-sized features that qualitatively support the above interpretation of the distributions obtained from the nuclear scattering as Figure 3 reveals. The volume distribution for $D < 16$ nm in the ODS Fe12Cr alloy has two modal peaks at ~ 6 and 12 nm, which practically coincide with those found for the distribution obtained from the nuclear scattering data.

It is worthwhile to remark that attempts for analyzing the present scattering data by the classic Guinier and Porod approximations, or using the unified approach and the Modeling II tools of the Irena 2.50 SAS macro package [17], failed to give realistic results.

3.2. *TEM observations and PALS measurements*

The presence of nanovoids, or small gas bubbles, with sizes smaller than 5 nm was previously detected by TEM in this same ODS Fe12Cr alloy [13]. In this study, the counterpart non-ODS alloy, i.e. the Fe12Cr alloy, was also explored by TEM and PALS in order to confirm the presence of these defects. Neither the through-focal analyses made by TEM nor the PALS measurements revealed the presence of nanovoids in the Fe12Cr samples in the as-HIP condition. After being heat treated at 1023 K, nanovoids with sizes below ~ 10 nm appeared as the TEM images in Fig. 4 show. In addition, a second lifetime component in the annihilation spectrum also appeared as the PALS results in Table 1 reveal. However, a lifetime of 259 ± 9 ps is significantly smaller than the expected positron lifetimes in nanovoids, or small gas bubbles, and therefore other defects with a higher number density seem to be mainly responsible for the second lifetime component.

The lifetime of the second component of the annihilation spectra, τ_2 , corresponds

with an annihilation signal coming from positrons trapped in vacancy-type defects. It depends on the atom density at the defect, and is representative of the nature and size of the defect, while its intensity I_2 is related with the number density of these defects.

Vacancy clusters and nanovoids in Fe and steels exhibit typical τ_2 values between 200 and 400 ps. In particular, τ_2 values between 240 and 340 ps in an ODS EUROFER steel were attributed to nanovoids and Ar-decorated voids, or small gas bubbles, induced by the processing of the material [19]. Furthermore, calculi in bcc Fe have predicted the τ_2 value as a function of the number of vacancies in tridimensional vacancy clusters, or nanovoids [20-23]. More details about the positron annihilation characteristics in ODS steels can be found in Refs. [19, 24]. The analyses of the lifetime spectra yield τ_1 and I_1 values inconsistent with those predicted by a two-state trapping model, if the lifetime for a free positron in the matrix is assumed to be ~ 110 ps, i.e. the expected lifetime for free positrons in α -Fe. In fact, it is expected that there exists more than one type of defects acting as positron traps in these samples. Thus, this first lifetime component, as well as the single lifetime component in the case of the non-ODS alloy in the as-HIP condition, reflects a resultant lifetime from annihilation events in the bulk and structural defects such as dislocations, vacancy-impurity complex defects and other defects associated to carbide precipitates, dispersoids, grain boundaries and particle/matrix interfaces. For the present discussion only the second lifetime component due to tridimensional vacancy clusters is actually of interest. τ_2 values in the range 200 – 260 ps indicate vacancy clusters containing between 2 and 6 vacancies in Fe [20-24]. For these vacancy clusters in Fe, the expected diameters have to be lesser than ~ 1 nm according to Ref. [25]. These sizes are below the length scales resolvable by the present SANS measurements.

Therefore, a consequent contribution of these vacancy clusters to the experimental

scattering curves would be meaningless.

It should be mentioned that a second positron lifetime in the same value range has also been found in an ODS Fe14Cr WTi alloy and attributed to positron trapping in Y-O rich dispersoids [26], or to vacancy clusters and Y₂O₃ particles [24]. The present results suggest that this second lifetime component may not be exclusively attributed to positron lifetime in the Y₂O₃ lattice because: i) PALS measurements performed on several Y₂O₃ single crystals yielded a single-component spectrum with a lifetime between 200 and 190 ps depending on the coloration of the single crystals, i.e. the content of point defects (colour centres) induced by inherent impurities [27]; and ii) a second lifetime component appears in Fe12Cr after heating at 1023 K that is analogous to the one in the heat treated ODS Fe12Cr alloy, see Table 1. Then, the development of this second lifetime component in the ODS and non-ODS alloys appears to be induced by thermal release of vacancies from complex defects and subsequent clustering into strong vacancy sinks associated with some of the microstructural features present in these alloys. The fact that the intensity of the second lifetime component for the ODS Fe12Cr alloy is twice the one for the non-ODS alloy may be interpreted as evidence for the development of vacancy clusters associated with the Y-O-rich dispersoids. However, other features not related with the Y oxide dispersion that exist in the alloy can also nucleate vacancy clusters. These may be the Cr-rich features already detected by TEM in these alloys [2]. Hence, these nanofeatures, i.e. Y oxide and Cr-rich nanoparticles, after thermal vacancy trapping turn into strong positron traps having an positron lifetime of 240 – 250 ps. Whether the vacancies develop vacancy clusters, or vacancy cluster-impurity complexes, at the particle/matrix interface or within the particles cannot be determined. In either case, the structure and/or chemical composition of the nanoparticles may change, i.e. the Y oxide nanoparticles could no longer be really Y₂O₃ but a complex oxide feature or vacancy-

atom cluster. In fact, it was found in Fe^{4+} irradiated samples of the present alloys that irradiation vacancy clusters appear to be associated with Cr atoms [28].

In principle, the evident presence of nanovoids, or gas bubbles, in the ODS Fe12Cr alloy, and the heat treatment effect on the τ_2 and I_2 values would suggest to associate these nanovoids with the distributions with mode at ~ 6 nm in spite of the incompatibility of their sizes with the τ_2 values measured, which are consistent with vacancy clusters of less of 1 nm. Nevertheless, the positron lifetime in voids with sizes of several nanometers containing gas entrapped can result in τ_2 values considerably smaller than the corresponding for the empty void [29, 30]. In the present work, the mechanical alloying was carried out in Ar. Thus, this second component in the positron lifetime spectra can be attributed to the presence of tridimensional vacancy clusters as well as the observed nanovoids that could contain Ar entrapped. In the case of the as-HIP Fe12Cr alloy, where nanovoids were not detected, the transformation of the distribution with mode at ~ 7 nm after the heat treatment in other with mode at ~ 6 nm can be tentatively explained by the thermal activated release of vacancies from impurity-vacancy complexes or atom clusters, or from structural defects such as dislocation tangles, grain boundaries, interfaces,etc, followed by formation of vacancy clusters, Ar-decorated nanovoids and/or gas bubbles.

3.3. *Quantitative analysis of the nano-sized features*

The assessment of the volume fraction, f_v , and number density of scattering centres, N , requires knowing their precise composition and structure for obtaining the scattering contrast $\Delta\eta = (\eta^c - \eta^m)$. The corresponding scattering length densities for the centres, η^c , and the matrix, η^m , can be evaluated by

$$\eta = \sum_i \frac{b_i X_i}{\Omega} \quad (5)$$

where b_i and X_i respectively represent the isotope averaged nuclear, or magnetic, scattering length and the atom fraction for the i element, and Ω the mean atomic volume. As the Y-rich particles are expected not to be ferromagnetic, the composition of these scattering centres would not be needed for evaluating the f_v and N if the volume distributions obtained from the magnetic scattering data are used. In this case, $\Delta\eta_{\text{mag}} = \eta_{\text{mag}}^{\text{m}}$. The magnetic scattering length for the matrix is evaluated according to Ref. [9] using a mean atomic magnetic moment for the matrix estimated from the magnetic data reported for alloys Fe-Cr as function of the Cr content [31]. To estimate f_v and N from the nuclear scattering data, it is assumed that all the Y-rich centres are monoclinic Y_2O_3 since this is the most frequent phase found for these centres, although other compositions have also been reported in these ODS alloys [2]. The used $\Delta\eta^2$ and the corresponding f_v and N values calculated for the nano-sized features are summarised in Tables 1 and 2 along with the mode and the cubic average diameter $D_{\langle V \rangle} = \langle D_V^3 \rangle^{1/3}$ obtained from the mean volume of the particles. It should be noted that the contrast for the matrix is calculated according to the composition previously measured by APT for these alloys in the as-HIP condition and after being heat treated since the transformation of Fe_xC carbides into M_{23}C_6 by the thermal treatment produces a considerable Cr depletion in the matrix [2]. The number density N of the scattering centres associated with the nano-sized features reflected by each modal peak is calculated by the equation

$$N = \frac{6f_v}{\pi D_{\langle V \rangle}^3} \quad (6)$$

The volume fractions and the number densities of scattering centres associated with the modal peaks at $\sim 12 - 14$ nm, calculated using the contrast values corresponding to

Y_2O_3 , are summarised in Table 2. The estimated fraction and number density of scattering centres are respectively found between 0.70 – 1.6 vol% and $0.74 \times 10^{22} - 1.72 \times 10^{22} \text{ m}^{-3}$, which is within the range of values obtained from TEM studies in this same ODS alloy, i.e. 0.14 – 2.3 vol% and $0.45 \times 10^{22} - 12 \times 10^{22} \text{ m}^{-3}$ [2]. As the f_v value obtained from the magnetic scattering should not be subjected to uncertainties coming from the chemical composition of the centres, these f_v values and the corresponding number densities are expected to be more accurate than those obtained from the nuclear scattering when an even structure and composition for the Y-rich centres, i.e. for the centres with modal values at $\sim 12 - 14 \text{ nm}$, is assumed. In the present ODS Fe12Cr alloy, part of these centres has been recognized as monoclinic Y_2O_3 ($\sim 30 \%$) or orthorhombic YCrO_3 ($\sim 10 \%$), but many others could not be unambiguously identified [2]. Nevertheless, it has been found that in the case of the as-HIP ODS alloy some metastable Fe_xC carbides or other unknown phases also appear to contribute to the modal peaks attributed to Y-rich centres, as shown in Figures 2 and 3 by comparison of the respective volume distributions for the ODS Fe12Cr and Fe12Cr alloys. After removing this contribution by effect of the heat treatment, the volume distribution from the magnetic scattering should provide more accurate f_v and modal values for the Y-rich particles. Then, the volume fraction of $0.70 \pm 0.03 \%$ calculated for the modal peak at 12.0 nm observed in the volume distribution obtained from the magnetic scattering is considered a better estimation for the Y-rich centres than the values obtained from the nuclear scattering data, see Table 2. It is worth observing that the nominal Y_2O_3 content of 0.40 wt% in the ODS alloy is equivalent to a volume fraction of 0.50 vol%, which should be the highest fraction of Y_2O_3 precipitates expected in the ODS alloy. However, a higher fraction of Y-rich particles would be expected since the TEM and APT analyses of the Y-rich particles performed on samples of this alloy revealed a frequent presence of Cr in these particles.

The discrepancies between the results from the nuclear scattering data and the ones from the magnetic scattering could be due to the simplified evaluation of the scattering contrast as well as differences between the chemical size inferred from the nuclear scattering and the size representing the magnetic hole of the corresponding centre. For instance, in the as-HIP ODS Fe12Cr alloy the fraction of scattering centres associated with the modal peak at $\sim 12\text{-}14\text{ nm}$, calculated from the nuclear scattering, is $1.02 \pm 0.11\text{ vol\%}$ but it is $1.6 \pm 0.3\text{ vol\%}$ when magnetic scattering data are used, see Table 2. This can be interpreted as evidence for the contribution of centres with a chemical composition different than the assumed one, which may have a smaller nuclear contrast. In fact, small Cr-rich particles with sizes similar to the Y-rich particles, or even smaller, were detected by TEM, so that some overlapping in the volume distribution of both type of particles is expected, see Figure 4 and Ref. [2].

Now, the results for the nano-sized features corresponding to the modal peaks at $\sim 6\text{--}8\text{ nm}$ will be discussed. First, it was assumed that these features might have a scattering contrast corresponding to holes in the matrix since PALS measurements and TEM analyses reveal the presence of nanovoids in the ODS Fe12Cr and heat treated Fe12Cr alloys, although not for the Fe12Cr alloy in the as-HIP condition where the peak is also present. The number densities of these features in the ODS alloy evaluated from the nuclear scattering data, as empty hole, result to be one order of magnitude lower than those determined from the magnetic scattering, see Table 1. Also, small Cr-rich particles with Cr_2O_3 compositions evidenced by TEM (see Figure 4), and simple Cr atom clusters, were considered as other plausible features to make an estimation of the number density of centres contributing to these modal peaks in the nuclear scattering curves. The results are summarised in Table 1. The assumption of being exclusively scattering from Cr-rich oxides results in a number density inconsistent with the one obtained from the magnetic

scattering. The absence of nanovoids in the as-HIP Fe12Cr alloy, in coincidence with the presence of the modal peak at $\sim 7 - 8$ nm, supports the existence of other nano-features contributing to the distribution at ~ 6 nm in the ODS alloy, besides nanovoids or gas bubbles. It should be noted that the heat treatment at 1023 K did not induce meaningful changes in the volume fraction and number density of centres of the ODS Fe12Cr alloy, neither in their size distribution, but it did in the counterpart non-ODS alloy. Regarding this discrepancy one should be aware that the characteristics and size distribution of the secondary phases not associated with Y are controlled by the milling conditions. The milling time for the Fe12Cr alloy was 15 h against 27 h for the ODS Fe12Cr alloy [2]. This may have resulted in secondary phases with different compositions and somewhat larger particle sizes for the Fe12Cr alloy as the results reflect. For instance, incomplete Cr solution could have resulted in the Fe12Cr alloy in the as-HIP condition giving rise to presence of Cr clusters, besides small metastable carbides. These scattering centres can be in part dissolved after heating at 1023 K for 4 h, or transformed into others with different composition. This would give account for the remarkable reduction of the volume fraction and number density values obtained from the magnetic scattering data after the heat treatment.

The analysis of the A ratio as a function of Q can give some insight on the composition of the nanosized features supporting the above results and discussion. The A values given by Equation (3) are represented in Figure 5. The A ratio for either alloys in the as-HIP condition is Q dependent over the whole Q range but the heat treatment at 1023 K produces a qualitative change. For both alloys, the A value turns into constant at 2.95 ± 0.12 over the interval $0.007 < Q < 0.032 \text{ \AA}^{-1}$. Assuming for the heat treated matrix $(\Delta\eta_{\text{mag}})^2 = 19.65 \times 10^{20} \text{ cm}^{-4}$, Equation (3) yields $(\Delta\eta_{\text{nuc}})^2 = (10.1 \pm 0.6) \times 10^{20} \text{ cm}^{-4}$, which is comparable with the values calculated for carbides such as Cr_7C_3 (8.684

$\times 10^{20} \text{ cm}^{-4}$) and Cr_{23}C_6 ($12.89 \times 10^{20} \text{ cm}^{-4}$). Since the M_{23}C_6 may have a substantial content of Fe and it lowers the nuclear contrast, the scattering centres in the mentioned interval of Q values, i.e. the large size centres, might be Cr_7C_3 or M_{23}C_6 carbides with the specific Fe content resulting in a nuclear contrast of $\sim 10.1 \times 10^{20} \text{ cm}^{-4}$. For $Q > 0.036 \text{ \AA}^{-1}$, the A ratio decreases continuously in the heat treated ODS Fe12Cr alloy indicating the presence of more than one type of scattering centres of small size. In contrast, the A values in the heat treated Fe12Cr alloy exhibit a constant value of 1.87 ± 0.14 for $Q > 0.065 \text{ \AA}^{-1}$ as Figure 5 reveals. Now, Equation (3) yields a value of $(\Delta\eta_{\text{nuc}})^2 = (23 \pm 4) \times 10^{20} \text{ cm}^{-4}$ very close to that calculated for Cr clusters ($21.01 \times 10^{20} \text{ cm}^{-4}$) but far away from the values for the other suggested phases (Cr_2O_3 and empty voids). The above would be compatible with the presence of Cr-rich nanoclusters in the heat treated non-ODS alloy suggesting their plausible presence in the heat treated ODS Fe12Cr alloy, although neither TEM nor APT analyses could confirm this assumption. In equilibrium, precipitation of Cr-rich phase in Fe-Cr alloys, like α' particles, is not expected for Cr contents below $\sim 12\text{wt}\%$. However, it can occur out of equilibrium according to irradiation results reported for these alloys [32]. The present ODS alloys have been produced by MA, where the system is driven out of thermal equilibrium attaining a super-saturation of lattice defects comparable to that induced by irradiation. PALS results have revealed the presence of defects resulting from vacancy agglomeration. These situation shares similarities with the behaviour of a material under irradiation, which could explain the presence of Cr-rich nanoclusters in the alloys as SANS results suggest.

Other compositions for Cr-rich particles suggested by previous TEM analyses from these alloys, such as Cr_2N and Cr_3C_2 , yielded completely unrealistic results.

3. Conclusions

The nano-sized features present in the ODS Fe12Cr (0.40wt%Y₂O₃) alloy and its non-ODS counterpart have been investigated by SANS in conjunction with PALS and TEM. The following main conclusions have been attained:

- i. The analysis of the nuclear and magnetic scattering data by the maximum entropy approach yields volume distributions, which interpreted in combination with PALS and TEM results, have allowed accomplishing a reasonable characterization of the scattering centres with sizes below ~ 16 nm.
- ii. The ODS alloy exhibits a volume distribution of particles with modal value at ~ 12 – 14 nm that are associated with the presence of Y-rich particles. This distribution appears not to undergo apparent changes after a heat treatment at 1023 K. From the quantitative analysis of the distributions obtained from the magnetic scattering, the volume fraction and number density of these dispersoids in the heat treated sample are respectively estimated in 0.70 vol % and $0.77 \times 10^{22} \text{ m}^{-3}$. These values are in agreement with the results from TEM measurements previously reported for the same ODS alloy.
- iii. In addition, another volume distribution with a modal value between 6 and 8 nm is found in both alloys. The presence of nanovoids containing Ar, or gas bubbles, in the ODS alloy, and their formation in the non-ODS alloy by effect of the heat treatment at 1023 K, point out the contribution of nanovoids/gas-bubbles to these volume distributions. Nevertheless, their quantitative analysis have revealed signs compatible with the presence of some other overlapped features which would really be the main centres contributing to this modal peak.
- iv. The measured A-ratio values are compatible with the presence of M₇C₃ and/or M₂₃C₆ carbides with sizes between 30 and 300 nm in both alloys after being heat

treated at 1023 K. In the case of the heat treated Fe₁₂Cr alloy, the A-ratio would indicate the presence of Cr clusters with a modal size of ~6 nm, which is attributed to the imperfect Cr solution.

- v. The analyses of the SANS data applying the classic Guinier and Porod approximations, or the unified approach, failed to yield results consistent with the microstructural results obtained from TEM, APT and PALS.

In the light of the present results, one should be aware that knowing the complex microstructure of the ODS Fe-Cr alloys, the analysis and interpretation of the SANS measurements in ODS Fe-Cr alloys cannot be as simple as it has been so far.

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Table and table captions

Table 1. Quantitative analysis of the distributions corresponding to the common nano-sized features found in the ODS Fe12Cr alloy and its non-ODS counterpart, and effect of the heat treatment at 1023 K on their positron annihilation parameters.

Table 2. Quantitative analysis of the modal peak attributed to Y-rich scattering centres in the ODS Fe12Cr alloy obtained from the nuclear and magnetic scattering data.

Figure captions

Figure 1. Nuclear and magnetic scattering intensity corrected after incoherent background subtraction for the ODS Fe12Cr and Fe12Cr alloys. The lines represent the maximum entropy fits.

Figure 2. Effect of the heat treatment at 1023 K on the particle volume distribution obtained from the nuclear scattering data for the ODS Fe12Cr and Fe12Cr alloys.

Figure 3. Effect of the heat treatment at 1023 K on the particle volume distribution obtained from the magnetic scattering data for the ODS Fe12Cr and Fe12Cr alloys.

Figure 4. Through-focal series of nanovoids (black arrows) and Cr-rich nanoparticles (white arrows) in the non-ODS Fe12Cr alloy. (a) Underfocused by 1 μm , (b) in-focus, (c) overfocused by 1 μm .

Figure 5. A-ratio values as a function of the scattering vector Q for the ODS Fe12Cr and Fe12Cr alloys.

Table 1. Quantitative analysis of the distributions corresponding to the common nano-sized features found in the ODS Fe12Cr alloy and its non-ODS counterpart, and effect of the heat treatment at 1023 K on the positron annihilation parameters of these alloys.

		Common nano-sized features					Positron lifetime measurements				
		Mode nm	D _v nm	Contrast (Δη) ² ×10 ²⁰ cm ⁻⁴	Volume fraction (%)	N ×10 ²² m ⁻³	τ ₁ ps	τ ₂ ps	I ₂ %	⟨τ⟩ ps	
O S F 12Cr	-HIP	Nuclear scatt.	6.1	6.4	56.62 (voids)	0.30±0.02	2.17	138±11	203±6	64±9	180
					5.690 (Cr ₂ O ₃)	3.0±0.2	21.63				
					21.01 (Cr)	0.81±0.6	5.86				
	Magnetic scatt.	6.6	6.7	19.02	2.1±0.3	13.33					
				Non magnetic phases							
	Heat treated	Nuclear scatt.	6.7	6.7	57.77 (voids)	0.30±0.02	1.91				
					6.058 (Cr ₂ O ₃)	2.9±0.2	18.41				
					21.01 (Cr)	0.83±0.06	5.27				
	Magnetic scatt.	6.3	6.4	19.65	2.0±0.4	14.57					
				Non magnetic phases							
As- P	Nuclear scatt.	7.2	7.2	56.62 (voids)	0.07±0.03	0.34					
				5.690 (Cr ₂ O ₃)	0.7±0.3	3.35					
				21.01 (Cr)	0.18±0.07	0.91					
	Magnetic scatt.	7.7	8.0	19.02	0.65±0.11	2.42					
				Non magnetic phases							
Heat treate	Nuclear scatt.	6.3	6.3	57.77 (voids)	0.034±0.007	0.26					
				6.058 (Cr ₂ O ₃)	0.32±0.06	2.50					
				21.01 (Cr)	0.093±0.018	0.72					
	Magnetic scatt.	6.7	6.8	19.65	0.03±0.03	0.18					
				Non magnetic phases							

Table 2. Quantitative analysis of the modal peak attributed to Y-rich scattering centres in the ODS Fe12Cr alloy obtained from the nuclear and magnetic scattering data.

			Y-rich features			
	Mode	$D_{(v)}$ nm	Contrast $(\Delta\eta)^2$ $\times 10^{20} \text{ cm}^{-4}$	Volume fraction (%)	N $\times 10^{22} \text{ m}^{-3}$	
2Cr	As H P	13.6	13.8	Nuclear 7.28	1.02±0.11	0.74
		12.0	12.1	Magnetic 19.02	1.6±0.3	1.72
DS	Heat eated	13.0	13.1	Nuclear 7.69	0.808±0.006	0.69
		11.8	12.0	Magnetic 19.65	0.70±0.03	0.77

173x56mm (300 x 300 DPI)

			Common nano-sized features					Positron lifetime measurements			
			Mode nm	D _(v) nm	Contrast (Δη) ² ×10 ²⁰ cm ⁻⁴	Volume fraction (%)	N ×10 ²² m ⁻³	τ ₁ ps	τ ₂ ps	I ₂ %	⟨τ⟩ ps
ODS Fe12Cr	As-HIP	Nuclear scatt.	6.1	6.4	56.62 (voids) 5.690 (Cr ₂ O ₃) 21.01 (Cr)	0.30±0.02 3.0±0.2 0.81±0.6	2.17 21.63 5.86	138±11	203±6	64±9	180
		Magnetic scatt.	6.6	6.7	19.02 Non magnetic phases	2.1±0.3	13.33				
	Heat treated	Nuclear scatt.	6.7	6.7	57.77 (voids) 6.058 (Cr ₂ O ₃) 21.01 (Cr)	0.30±0.02 2.9±0.2 0.83±0.06	1.91 18.41 5.27	156±6	237±7	44±8	192
		Magnetic scatt.	6.3	6.4	19.65 Non magnetic phases	2.0±0.4	14.57				
Fe12Cr	As-HIP	Nuclear scatt.	7.2	7.2	56.62 (voids) 5.690 (Cr ₂ O ₃) 21.01 (Cr)	0.07±0.03 0.7±0.3 0.18±0.07	0.34 3.35 0.91	159±2			
		Magnetic scatt.	7.7	8.0	19.02 Non magnetic phases	0.65±0.11	2.42				
	Heat treated	Nuclear scatt.	6.3	6.3	57.77 (voids) 6.058 (Cr ₂ O ₃) 21.01 (Cr)	0.034±0.007 0.32±0.06 0.093±0.018	0.26 2.50 0.72	143±2	253±9	20±3	165
		Magnetic scatt.	6.7	6.8	19.65 Non magnetic phases	0.03±0.03	0.18				

			Y-rich features			
		Mode nm	$D_{\langle v \rangle}$ nm	Contrast $(\Delta\eta)^2$ $\times 10^{20} \text{ cm}^{-4}$	Volume fraction (%)	N $\times 10^{22} \text{ m}^{-3}$
ODS Fe12Cr	As-HIP	13.6	13.8	Nuclear 7.28	1.02±0.11	0.74
		12.0	12.1	Magnetic 19.02	1.6±0.3	1.72
	Heat treated	13.0	13.1	Nuclear 7.69	0.808±0.006	0.69
		11.8	12.0	Magnetic 19.65	0.70±0.03	0.77