Positron annihilation in neutron irradiated iron-based materials

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Abstract. The hardening and embrittlement of reactor pressure vessel steels is of great concern in the actual nuclear power plant life assessment. This embrittlement is caused by irradiation-induced damage, like vacancies, interstitials, solutes and their clusters. But the reason for the embrittlement of the material is not yet totally known. The real nature of the irradiation damage should thus be examined as well as its evolution in time. Positron annihilation spectroscopy has been shown to be a powerful method for analyzing some of these defects. In fact, both vacancy type clusters and precipitates can be visualized by positrons. Recently, at SCK•CEN, a new setup has been constructed, calibrated and optimized to measure the coincidence Doppler broadening and lifetime of neutron irradiated materials. To be able to compare the results obtained by the positron studies, with those of other techniques (such as transmission electron microscopy, atom probe tomography and small angle neutron scattering), quantitative estimations of the size and density of the annihilation sites are needed. Using the approach proposed by Vehanen et al., an attempt is made to calculate the needed quantities in Fe and Fe-Cu binary alloys that were neutron irradiated to different doses. The results obtained are discussed highlighting the difficulties in defining the annihilation centres even in these simple model alloys, in spite of using both lifetime and Doppler broadening measurements in the same samples.

1. Introduction

For the safe operation of the nuclear power plants (NPPs), it is mandatory to ensure the mechanical integrity of the reactor pressure vessels (RPV). This irreplaceable component is made of steels that are prone to embrittlement due to neutron irradiation. In fact, these neutrons, when colliding with the material, produce microstructural defects, such as vacancies, interstitials and their clusters. The abundance of these defects is the origin of irradiation-induced precipitation and segregation. Thus, the study of defect formation under neutron irradiation and their thermal stability is of paramount importance for the understanding of radiation damage of structural materials. Moreover, to extend the lifetime of the NPPs, there is an urgent need for predictive models based simultaneously on experiments and numerical computer simulation.

Irradiation-induced embrittlement can be summarized by three main causes [1], i.e. precipitation, matrix-damage and grain boundary segregation. The nature of these defects has to be known for the
better understanding of the interplay of hardening and embrittlement. However and up to now, it is still uncertain to assess the main mechanism that gives rise to the matrix-damage. Among others, Malerba [2] has shown that directly in the cascades some candidate cluster-solute complexes inducing small vacancy and interstitial clusters are produced. These defects aggregate to larger defects such as nano-voids and interstitial loops. At the same time, various solutes may diffuse to these clusters giving rise to complex defect-solute configurations.

PAS is found to give valuable information on these irradiation-induced defects [3]. In this technique, the positron is applied as probe. As anti-particle of the electron, the positron is trapped by defects with a different electron density than the bulk material, like vacancies, vacancy clusters, interfaces, second phase particles, dislocations, etc. [4]. The annihilation characteristics are different in the neighbourhood of defects compared to defect-free materials. Moreover, due to the difference in positron affinity of the different atoms, positrons annihilate with a different probability in the precipitates as compared to the bulk material [5]. The power of PAS is its possibility to find very small defects (> 0.1 nm) with very low concentrations (> 1 ppm), its "self-seeking" nature (the positron diffuses trough the matrix before it gets trapped [3]) and its non-destructiveness.

Significant insight into potential vacancy clusters has been made by PAS during the past decades [6]. Focus should now being put on the quantitative estimations of the average size and density of the annihilation sites, as this would lead to a better comparison with other techniques, such as transmission electron microscopy (TEM), atom probe tomography (APT) and small angle neutron scattering (SANS). On top of this, the quantitative determination of the defects is necessary for the production and validation of the predictive models.

Over the last 40 years a lot of investigations have been performed to determine the specific lifetime of positrons trapped at different types of defects in pure iron and Fe-based alloys. Experimentally, this has been done by recovery experiments of deformed iron [7], [8], as well as by the annealing of vacancies in electron irradiated iron [9], [10]. But, also models are produced to correlate a specific trapping site with the observed annihilation characteristics. While these calculations have been fairly successful for monovacancies in a wide variety of metals [11], they are not easily generalized to more complicated defect geometries.

In metallic systems, vacancies and small vacancy clusters show a well-defined relationship between the positron lifetime and the size of the open-volume region [12]. The local electron density determines the positron annihilation rate. Since the electron density is lower at an open-volume region compared to bulk material, the lifetime is increased for positrons trapped at vacancy clusters. The lifetime depends on the size of the open-volume region, so positron lifetime measurements can be used as a measure of the vacancy cluster size.

To interpret the experimental results, a theoretical model, which gives positron lifetime as function of micro-void size, is vital. Based upon a simple superimposed-atom model, Puska and Nieminen [13] have performed such calculations for positron lifetimes in micro-voids consisting of 1 (V1) tot 15 (V15) vacancies, using a fitting parameter to reproduce the experimental bulk lifetime. To examine larger micro-voids, however, ab-initio based superimposed-atom model calculations have been performed by Hempel et al. [14].

The above mentioned models are used to figure out how the size and density of the vacancy-type of defects that were produced in each of the neutron irradiated materials. Eldrup et al. [15] have already done such an attempt to extract the number density of microvoids present in pure Fe after neutron irradiation at 70 °C.

The present work consists on assessing the ageing mechanism of the reactor pressure vessel steels of old (generation II) nuclear reactors, which are in operation for more than 30 years. It is well known that these RPV-steels contain a considerable amount of copper impurities. Therefore, binary Fe-Cu alloys are often used to mimic their behaviour. Indeed, Fe-Cu model alloys show a similar increase in hardening during irradiation coming from the copper-rich precipitates [16]. Moreover, binary Fe-Cu alloys are chosen, to compare them with pure iron and iron containing a certain amount of carbon (as C plays an important role in steels). Finally, an attempt is made to calculate the needed quantities (i.e.
size and density of the irradiation-induced vacancy type of defects), using the approach proposed by Vehanen et al. [9], in pure iron and Fe-Cu binary alloys that were neutron irradiated to different doses.

2. Materials and irradiation conditions
The model alloys listed in table 1 were prepared using argon-arc melting and zone refinement methods, starting from electrolytic iron. The resulting ingots were cold worked after austenisation and tempering. A final heat treatment at 1075 K for 1 h was performed to release the stresses and to get well re-crystallized materials.

| Material | Nominal composition in wt% |
|----------|-----------------------------|
| Pure Fe  | < 30 ppm C                  |
| Fe-C     | > 30 ppm C                  |
| Fe-0.1% Cu | 0.1 Cu (< 30 ppm C)         |
| Fe-0.3% Cu | 0.3 Cu (< 30 ppm C)         |

Samples from each alloy were irradiated in the test reactor BR2 at SCK•CEN. Table 2 lists the neutron fluxes and the reached fluences. During irradiation the temperature and the pressure were maintained constant respectively in between 290 and 295 °C and at 150 bar. The four of the irradiation conditions have the same flux of about $9.5 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$, but different doses going from about 0.025 dpa to about 0.2 dpa. It is worth mentioning that at the highest flux of pressurised water reactors, 0.1 dpa corresponds to about 40 years of operation.

| Dose (dpa) | Flux ($10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$) | Fluence ($10^{19} \text{ n cm}^{-2}$) |
|------------|-----------------------------------------------|-----------------------------------|
| 0.026      | 9.36 ± 0.52                                  | 1.5 ± 0.7                         |
| 0.051      | 9.32 ± 0.55                                  | 3.0 ± 0.5                         |
| 0.1        | 9.54 ± 0.54                                  | 6.9 ± 0.5                         |
| 0.19       | 9.58 ± 0.52                                  | 12.5 ± 1.1                        |

3. Measurements and analysis
As the positron affinity for both vacancies and copper atoms is higher than the one of pure iron [5], PAS will be sensitive to these types of defects. Therefore, positron annihilation lifetime spectroscopy (PALS) and coincidence Doppler broadening spectroscopy (CDB), both available in the hot cell laboratory of SCK•CEN, have been used in a complementary way. PALS measurements give information on the electronic density of the material at the place of the annihilation. While, CDB spectroscopy allows measuring the momentum distribution of the electron-positron annihilated pair, giving information of the chemical environment surrounding the annihilation sites.

3.1. Positron lifetime measurements
Non- and irradiated specimens of $(10 \times 10 \times 1) \text{ mm}^3$, have been first surface polished to a mirror finish, and then chemically etched using a (HF + H₂O₂ + H₂O)-solution to remove the deformed surface layer. The specimens, taken two-by-two in a sandwich-like fashion, with the positron source in-between, were mounted in the specimen holder under biologically shielded environment. The sandwich was then automatically loaded (with a pneumatic loading system) in the measurement cell between three detectors working in anti-coincidence mode.
Measuring irradiated materials is proven to be more difficult, as care has to be taken to separate correctly the $\gamma$-peaks coming from the specimens and those related to the positrons. The setup used at SCK•CEN has been fully optimized for this purpose, as reported by Jardin et al. [17], [18]. Indeed, this triple coincidence setup was demonstrated to be very efficient in preventing the collection of the events due to $^{60}$Co, which is the main isotope produced by neutron activation, during the irradiation of the alloys under investigation. On top of this, the detectors are mounted such that the distance separating the detectors can be adjusted to minimize the background, depending on the radioactivity of the samples.

After the collection of a statistically sufficient amount of triple coincidence events, the newly developed software analyses the raw data of each event, and allows a clear visualization of the results. Four characteristics of every signal such as peak height, peak intensity, base level and rising time are determined. The appropriate value ranges are then selected to filter the signals within the defined energy-range, avoiding any pileup. Thus, only the signals satisfying the selected ranges are used for the generation of a positron lifetime spectrum. In order to achieve a statistically relevant number of counts (i.e. at least one million counts), the acquisition of each spectrum has required in-between a few days and about one month.

The analysis of the obtained spectra has been performed using the LT-software [19]. The resolution of the setup was constantly checked to be about 175 ps, while the source contribution was set to 15 % with a single lifetime of 393 ps. All measurements were performed at room temperature, using a $^{22}$Na source, with a strength of 2 MBq, wrapped in Kapton foils.

### 3.2. Coincidence Doppler broadening measurements

The CDB setup has been described with ample details by Verheyen et al. [20]. Here, both annihilation photons are detected in coincidence in order to minimize the background, [21], while the pileup is prevented, by making the detectors movable to larger distances from the sample (up to 1.5 m). The stability of the system was continuously checked, as a $^{57}$Co source was installed inside the setup. This source emits photons with energies of respectively 122 keV and 136 keV. These peaks are used in combination with the 511 keV peak to monitor the calibration and resolution simultaneously.

The specimen preparation and the loading of the specimen in the setup were done in a similar way, as it has been explained for the PALS measurements. The overall energy resolution was $\approx 1.07$ keV full width at half maximum (FWHM), which corresponds to the momentum resolution of $\approx 4.2 \times 10^{-3}$ $mc$ (FWHM). For each measurement, more than $1 \times 10^8$ counts were accumulated what takes 2 to 3 days of acquisition.

The analysis of the results has been made based on the selection of a channel across the coincidence region of the 2D-spectra obtained from the measurements. Thus, the resulted one dimensional spectrum from each sample was normalized to the one obtained for the unirradiated defect-free pure Fe. The as such obtained CDB ratio curves allow a clear description of the momentum distribution. Two parameters, $S$ and $W$, were extracted form each spectrum. These parameters are defined respectively as the ratio of low-momentum ($|cp_l| < 2.5 \times 10^{-3}$ mc) and high-momentum ($15 \times 10^{-3}$ mc $< |cp_l| < 25 \times 10^{-3}$ mc) regions in the CDB spectrum to the total region ($c$ is the speed of light and $p_l$ is the longitudinal component of the positron-electron momentum along the direction of the $\gamma$-ray emission).

### 4. Determination of the average size of the defects

As it was shown in section 1, the determination of the average size of the defects has been performed by many authors. In the following, all the results from literature are given and used with equal value.

#### 4.1. Pure Fe

In figure 1, the results found in literature are summarized. The available data can be separated in four groups. Each of them used a different approach to estimate the positron lifetime as function of the vacancy size. Group 1 contains papers from Vehanen, Hautojärvi, Puska and co-workers [7], [9], [10],...
Group 2 gives the results published by Nagai, Tang and co-workers [3], [8], [14], [24], [25]. Group 3 shows the data given by Kuriplach et al. [26]. And the results of group 4 were published by Asoka-Kumar and co-workers [27], [28]. However, from the figure, it could be seen that the same trend is observed from all published data. Especially, the results from group 2 and 3 are quite identical as they use a similar approach for their calculations. In this work, a general trend line has been estimated based on all literature data points. As it is shown in figure 1, this trend is pretty close to the most recent results of group 2 and 3, that were obtained using ab-initio type of calculations.

Figure 1. The results found in literature for the positron lifetime component of vacancy clusters with increasing amount of vacancies inside the clusters.

All calculations and experiments have of course been performed for pure iron. Adding alloying elements will lead to a shift of the above curve. As this shift depends on the amount of alloying elements at the annihilation sites, it is very difficult to determine the correct amount of vacancies inside the defect that gives rise to a particular lifetime component.

4.2. Fe-C
As for Fe doped with some C (the basic component of a steel), it is expected that the lifetime of vacancy clusters, combined with some carbon will change compared to the same pure vacancy clusters. In literature, however, two contradictory opinions have been found for the positron lifetime component of a carbon-vacancy pair. Hautojärvi et al. [23] found experimentally that this component should be equal to 160 ps (i.e. 15 ps less than the value of a monovacancy), while Asoka-Kumar et al. using his model [27] found that the addition of 1 carbon atom to 1 and 2 vacancies in Fe would lead to an increase of about 5 ps (i.e. 181 ps for the carbon-vacancy pair lifetime component).

As it is still questionable which of the two opinions is the most accurate, in this paper it is chosen to use the same values for the alloy containing some carbon as for the pure iron. Moreover, even for the pure iron differences of more than 10 ps have been found between the different groups for a cluster containing a certain amount of vacancies (see figure 1). On top of his, it should be mentioned that it is very difficult to determine experimentally if carbon is located near the annihilation site or not (see for instance [16]).
4.3. Fe-Cu

For the binary Fe-Cu alloys, it is expected that the lifetimes found for the vacancy clusters containing some copper will be different from the lifetimes found for the copper-free clusters. Indeed, Kuriplach et al. have shown that the lifetime component slightly decreases with increasing copper coverage of the vacancy clusters (see figure 2 of [26]).

As the presence of copper is well observed in the CDB curves, it is possible to estimate the amount of copper present at the annihilation sites, using the approach developed by Nagai et al. [29] and [25]. They found that the distribution in the binary Fe-Cu alloy can be approximately expressed in function of the distributions of pure iron and pure copper, as it is shown in (1), where \( N_X(p_L) \) represents the high-momentum distribution of the CDB spectrum of the alloy. In this equation, \( x \) is the coverage of the defects by copper atoms (i.e. the fraction of Cu atoms that substitute Fe atoms in the first shell surrounding the annihilation site).

\[
N_{Fe-Cu}(p_L) \propto (1-x) \cdot N_{Fe}(p_L) + x \cdot N_{Cu}(p_L)
\]

(1)

As the ratio curve is given by \( R_{X/Y}(p_L) = N_X(p_L)/N_Y(p_L) \), the ratio curve for the binary Fe-Cu alloy can be expressed with (2).

\[
R_{(Fe-Cu)/Fe}(p_L) \propto (1-x) + x \cdot R_{Cu/Fe}(p_L)
\]

(2)

Therefore, figure 2 plots the normalized CDB curves obtained for each irradiation condition of the two binary alloys investigated here. For comparison and illustration, the ratio curve for pure Cu normalized to pure Fe is also reported.

![Figure 2](image_url)

**Figure 2.** The CDB ratio curves for the binary Fe-Cu alloys at the different irradiation conditions. (a) shows the results for the Fe-0.1% Cu alloy and (b) those for the Fe-0.3% Cu alloy.

Figure 3 illustrates the estimated fractions of the positrons annihilating with copper electrons for the two Fe-Cu alloys after irradiation to the different doses. The estimated fractions are determined by fitting the Cu curve to the Fe-Cu curves, using (2) and taking into account the effect of vacancies who tend to increase the S parameter and decrease the high momentum region \( p_L > 7 \times 10^{-3} mc \). Thus, the \( x \)-parameter is varying between zero when no Cu atoms are surrounding the annihilation site and 1 when this first shell is entirely made of Cu atoms.

It is found that for the alloy containing 0.1 % of copper, the degree of coverage is very low, i.e. lower than 50 %, while for the alloy containing 0.3 % of copper, it increases to about 100 %. This is easily understood, as more copper is available in the latter alloy.
The copper in the alloys combines with the relatively small amount of vacancies, produced at low doses. With increasing irradiation dose, the degree of coverage decreases steadily, as more and more vacancies are available that can reach the already formed clusters.

Based on the obtained degree of coverage and using both the average lifetime of vacancies in pure iron from figure 1 and the results of Kuriplach et al. (see figure 2 of [26]), it becomes possible to identify the V-Cu clusters associated with the second component of the lifetime measured in the Fe-Cu alloys. In fact, these second lifetime component results of the PALS analysis can lead to an estimation of the average size of the clusters, including both the number of vacancies and those of copper atoms, co-clustering together. It should be noticed that an increasing amount of vacancies will lead to an important increase of the lifetime of the defect, while an increasing amount of copper atoms will slightly decrease this lifetime.

5. Determination of the concentration of annihilation sites

In order to extract the real properties of the defects, their size and density, from the experimentally obtained lifetime components and their associated intensities, the following well-known set of differential equations needs to be solved.

\[
\frac{d}{dt} n_B(t) = -\left(\lambda_B + \sum_{i=1}^{k} \kappa_i\right)n_B(t) + \sum_{i=1}^{k} \delta_i \cdot n_{D_i}(t) 
\]

\[
\frac{d}{dt} n_{D_i}(t) = \kappa_i \cdot n_B(t) - \left(\lambda_{D_i} + \delta_i\right) n_{D_i}(t) 
\]

Here, the quantities \( n_B(t) \) and \( n_{D_i}(t) \) are the densities of the positrons in respectively the bulk and the defect state at time \( t \), while \( \lambda \) is the annihilation rate, \( \kappa \) is the trapping rate and \( \delta \) is the detrapping rate. The indices \( B \) and \( D_i \) denote the free (bulk) and the trapped (defect) state, respectively. It should be mentioned at this point that the detrapping rate is considered to be negligible in most cases compared to annihilation and trapping rates [22].

In most cases, only one trapping state is used (i.e. \( k \) is equal to 1). But this situation cannot be applied for irradiated samples, as more than one trapping site is expected. Nevertheless, for the pure iron and the Fe-C alloy irradiated at low flux, reasonable values for \( \tau_i \) have been found with a single
trapping model. In all other cases a second trapping state had to be included, as it is illustrated in figure 4. For this model, a 3-component analysis of the lifetime spectrum is required, however, in this work, a 2-component analysis gave a fairly sufficient fitting of the obtained spectra, while the analysis with 3 components failed to converge to singular results. Therefore, and in order to comply with the model, one of the experimentally obtained components should be considered as a combination of two components. In this work, it is assumed that the experimental first component fulfils this role. In fact, these first lifetime components are found to be in-between 90 and 120 ps, and therefore they are much higher than what is expected for a polycrystalline Fe alloy. Indeed, \( \tau_{1,\text{exp}} \) is expected to be equal to \( \tau_{1,\text{calc}} \), given by (5). This equation shows that \( \tau_{1,\text{exp}} \) should be lower than the bulk lifetime, \( \tau_B \), which is equal to 107 ps.

\[
\tau_{1,\text{calc}} = \left( \lambda_{1,\text{calc}} \right)^{-1} = \left( \lambda_B + \kappa_1 + \kappa_2 \right)^{-1}
\]

(5)

Figure 4. Two types of defect traps are assumed, i.e. short lifetime traps and clusters. The lifetime of the short lifetime traps is supposed to be experimentally measured as part of the first component.

It is thus supposed that the lifetime of the short lifetime traps is experimentally measured as part of the first component, as illustrated in figure 4. This has been firstly introduced by Vehanen et al. [9] and in the present work the formulae proposed by Vehanen et al. (6) and (7) will be applied. Also here, \( \tau_{1,\text{calc}} \) is given by (5). For clarity, from now on the short lifetime traps will be denoted as \( \text{sh} \), while the traps with longer lifetimes are named clusters (\( \text{cl} \)).

\[
\begin{align*}
I_{1,\text{exp}} &= I_{1,\text{calc}} + I_{\text{sh}} \\
I_{2,\text{exp}} &= I_{\text{cl}} \\
\tau_{1,\text{exp}} &= \frac{I_{1,\text{calc}} \cdot \tau_{1,\text{calc}} + I_{\text{sh}} \cdot \tau_{\text{sh}}}{I_{1,\text{calc}} + I_{\text{sh}}} \\
\tau_{2,\text{exp}} &= \tau_{\text{cl}}
\end{align*}
\]

(6) (7)

With the equations given by (6) and (7) and the fact that \( I_{1,\text{exp}} + I_{2,\text{exp}} = 1 \), only five equations are available to calculate six unknown parameters. Therefore, one of the parameters should be determined by another way. In this respect, a parametric study has been performed to determine the best value for \( \tau_{\text{sh}} \). Figure 5 shows the estimated defect densities for both the short lifetime traps (figure 5 (a)) and the clusters (figure 5 (b)), estimated using the equations given before, inserting the experimental results for irradiated pure iron, as well as a fixed value for \( \tau_{\text{sh}} \). These calculations have been performed for different values for \( \tau_{\text{sh}} \), changing from 120 ps to 175 ps, with an interval of 5 ps, using as input values those provided by Vehanen et al. [9]. The results shown here were carried out for the pure iron experiments, but they were also performed for the other alloys, with comparable results.
The estimated densities for both the short lifetime traps and the clusters show unjustified trends for very low values of $\tau_{sh}$, while the results for high values of $\tau_{sh}$ are converging to reasonable values. In order to keep the differences as small as possible, only the high values of $\tau_{sh}$ were taken into account.

More precisely, the ranges are chosen between 150 ps and 175 ps for the densities of the short lifetime traps and between 140 ps and 175 ps for the densities of the clusters.

More information is needed to select the best value for $\tau_{sh}$. Asoka-Kumar et al. [27] has found that the value of the lifetime for a dislocation combined with a vacancy is in-between 142 and 165 ps. While, as mentioned earlier, Hautojarvi et al. [23] found a lifetime of 160 ps for a V-C pair. Furthermore, for the alloys containing copper, it has been argued in section 4.3, that the lifetime component for vacancies combined with copper is lower than the single vacancy lifetime in Fe (i.e. 175 ps). It is therefore obvious that for the short lifetime traps in the Fe-based alloys, a value of 160 ps should be assigned in our case, whatever their origin is.

Now, with a fixed $\tau_{sh}$, it is possible to solve the differential equations given by (3) and (4) and therefore determine all other parameters. The defect density of both the short lifetime traps $c_{sh}$ and the clusters $c_{cl}$ can be estimated, using (8).

$$
\begin{align*}
K_{sh} &= \mu_{sh} \cdot c_{sh} \\
K_{cl} &= \mu_{cl} \cdot c_{cl}
\end{align*}
$$

The specific trapping rate for monovacancies $\mu_V$ has been determined by Vehanen et al. [9], to be equal to $(1.1 \pm 0.2) \times 10^{15} \text{s}^{-1}$. The same specific trapping rate of single vacancies is used for the short lifetime traps ($\mu_{sh} = \mu_V$), as they are, as mentioned earlier, considered to be most probably composed of single vacancies associated with a foreign element or a dislocation.

As for the clusters, unfortunately, no experimental data are available on their specific trapping rate $\mu_{cl}$. On top of this, Nieminen et al. [30] have shown that lifetime measurements exhibit strong temperature dependence for the positron trapping probability at large voids in aluminium. In addition, they showed that the specific trapping depends linearly on the temperature, in the case of large voids at low temperatures, as the trapping process is transition limited (the positron mobility is large and the capture rate is small). At temperature above 200 K, however, the process becomes diffusion limited and the dependence on temperature becomes weak. The same has been observed for an iron-based alloy containing voids with a lifetime of 500 ps by Huguenin and Moser [31], ten years later. However, in the latter work, the authors suggest that the variations under consideration are strongly dependent on void size. For small vacancy clusters (with a lifetime of 260 ps), no temperature variation could be detected in the samples. In the alloys investigated in the present work, the clusters

**Figure 5.** The estimated defect density for respectively the short lifetime traps (a) and the long lifetime traps, i.e. the clusters (b) are shown with changing assumption for the value of $\tau_{sh}$. $\tau_{sh}$ varies from 120 ps to 175 ps for both calculations.
have been observed to be small [16], with a lifetime comparable to the one given by [31]. Therefore, it can therefore be assumed that the dependency on temperature of the specific trapping rate of the clusters found here is negligible. On the other hand, theoretical calculations by Nieminen and Laakkonen [32] indicated that for these small vacancy clusters in metals, the positron trapping rate is proportional to the defect volume, i.e. the number of vacancies in the cluster \( N \), given by 
\[
\mu_{cl} \approx \mu_v \cdot \frac{N}{V}
\]

6. Results and discussions
The results have been qualitatively explained in previous papers [16], [33]. In the present paper, an attempt is made to extract quantitative information on the detected defects. It is worth mentioning at this point, that although the lifetime results obtained show rather high reproducibility and low uncertainties (i.e. less than 5 ps), the estimated sizes and densities depicted below are to be considered in conjunction with the assumptions and the model used.

6.1. Pure Fe and Fe-C
Using the obtained lifetime results, reported in [33], the average size of the clusters and the number density of both the clusters (red curve) and the short lifetime traps (blue curves) are reported, as function of the irradiation dose, in figure 6 for pure iron and in figure 7 for the Fe-C alloy, as estimated following the methodology described above.

![Figure 6. The estimated values for the size and density of the defects in the pure Fe alloy.](image)

![Figure 7. The estimated values for the size and density of the defects in the Fe-C alloy.](image)

For pure iron, it is observed that the size of the clusters increases gradually with the irradiation dose, while the number density of the clusters decreases. The clusters thus grow by agglomeration of smaller clusters. With increasing the irradiation dose, the newly produced vacancies will be distributed between the clusters and the bulk. Indeed, the density of the short lifetime traps increases as well as the size of the clusters. As it was found that the density of the clusters diminish with dose, it is (as
mentioned before) understandable that the amount of vacancies, which are still present in the bulk, increases.

The estimated diameter given in figure 6 agrees mainly with the one observed by Eldrup et al. (see figure 4 of [15]) for pure iron irradiated to approximately the same dose. The number density of the defects published by Eldrup et al. (see figure 5 of [15]), on the other side, is about 10 times higher than the one found here. This might be the effect of the irradiation temperature, as the alloys in the paper of Eldrup et al. were irradiated at 70 °C, while in the current paper the irradiation temperature was 300 °C. Indeed, at higher temperatures, more vacancies and small vacancy-clusters will be more mobile, decreasing the amount of clusters.

When carbon is added to the alloy, the size of the clusters is smaller than in pure iron. In fact, carbon hinders the growth of the clusters. This size also seems almost to saturate at higher doses. The density of both the short lifetime traps and the clusters show a peak at about 0.025 dpa. This can be caused by the presence of carbon. The vacancy-carbon pairs are rather stable [34] and the agglomeration will only start after supersaturation of vacancies. After they are formed, they grow until about 5 vacancies and then stabilize again. Newly produced vacancies will especially be present in the bulk material, combined again with the carbon, but also some new clusters will be formed.

6.2. Binary Fe-Cu alloys

As for these alloys, the results for the average size of the clusters and the number density of both the clusters and the short lifetime traps are given in figure 8 for the Fe-0.1% Cu alloy and in figure 9 for the Fe-0.3% Cu alloy. Here it is assumed that the clusters are spherical Cu-V co-clusters where the vacancies are in fact covered by Cu atoms. In red, the average size of the clusters is expressed as the average number of vacancies in the clusters, while the curve in purple is the apparent size of the clusters, including both vacancies and Cu-atoms (i.e. the degree of copper coverage is added to the values in red).

Figure 8. The estimated values for the size and density of the defects in the Fe-0.1% Cu alloy. Figure 9. The estimated values for the size and density of the defects in the Fe-0.3% Cu alloy.
In the alloy containing 0.1 wt% of copper, the vacancy clusters seem to be very stable with dose. Nevertheless, a decrease of number density is found after about 0.05 dpa. This is most probably due to the agglomeration of the small clusters. Thereafter, the amount of clusters remains almost constant. Newly produced vacancies will thus be trapped by the clusters, as proposed by Verheyen et al. [20]. Indeed, the number of short lifetime traps is constant after 0.05 dpa, while the size of the clusters seems to grow very gently.

For the alloy containing 0.3 wt% of copper, the same observation can be made, except that the number density of both short lifetime traps and clusters keeps on growing with irradiation dose. This indicates that there is still copper available in the matrix with which new clusters and short lifetime traps are formed. As more clusters (and short lifetime traps) can be formed in this alloy, the clusters will remain smaller in term of the included amount of vacancies. Nevertheless, the total V-Cu clusters will be bigger due to a larger amount of copper atoms.

6.3. Comparison with other techniques

In figure 10, the results obtained by Meslin et al. [35] from four different microstructural techniques, that examine the same samples, are reported for the dose of 0.1 dpa. All measurements were performed within the European PERFECT project [36]. Each technique provides the number density and the mean size of the microstructural feature to which it is sensitive [16].

![Figure 10](image)

**Figure 10.** The estimated values for the size and density of the defects, found for 4 different techniques.

The objects detected by APT are unambiguously known to be precipitates, whose composition is reliably provided by the technique. Nevertheless, APT cannot detect the presence of vacancies associated with the observed precipitates, if they are present. The precipitate sizes obtained from the
APT are apparent and they do not include the very small vacancy-solute clusters, containing only few vacancies and solute atoms.

The SANS defects appear to give bigger mean sizes than it is observed by APT, while their number density is a little lower. This can be explained by the fact that very small defects, resolvable by APT, were not detected by SANS. Nevertheless, APT and SANS results are still in good agreement, and it can therefore be assumed that they correspond to the same defect populations.

The defects, visible by TEM, on the other hand, do not correspond to any of the previous categories. These defects are known to be mainly self-interstitial loops, limited to those of size larger than 2 nm. Indeed, defects smaller than 2 nm are coherent with the matrix, and therefore not detected by TEM. As these defects were not observed by any other technique, the TEM results are needed for a full picture of the defects.

Finally, the average size obtained from the lifetime measurement with PAS reflects the amount of vacancies and, if present, copper atoms. However, one should expect an important size distribution due to the stochastic character of neutron irradiation. It is thus obvious that PAS cannot detect all the clusters especially the ones with very low density (mostly the larger ones). At the same time, with positrons it is possible to see all kind of defects containing vacancies, even only a few vacancies close to foreign elements are detectable. These types of defects cannot be resolved by any other technique. So, the defect population detected by PAS is understood to correspond to small vacancy clusters and voids, associated or not with solute atoms.

The results obtained by Eldrup et al. for the density of defects in pure iron alloys irradiated up to the same dose (see figure 5 of [15]) are very comparable with ours, as they also found about 2 order of magnitude difference in-between the values given by TEM and those given by PAS. This indicates that the results that were obtained here are very reasonable.

The combination of the four experimental techniques for microstructural characterization leads to a good comprehension of all defect populations created by irradiation inside the model alloys. A sensible assessment of the strength associated with the different defect population, using the Orowan equation for each contribution, and their combination using the proper superposition law, provides a reasonable rationalization of the hardening results, as it has been done in [37].

7. Conclusions and outlook
An attempt to extract numerical information on the defects detected by PAS has been made based on the existing knowledge of the interaction between positrons and vacancy type of defects in Fe. It is thus demonstrated that using an educated guess, it is possible to access to the most useful information about the neutron irradiation induced defects, namely size and density of the trapping sites.

It was shown that in Fe, the average size of the defects observed can be estimated using a reasonable assessment of the literature data, but in binary alloys, such as Fe-Cu, a special care should be taken for the degree of copper coverage of the vacancy clusters. The latter could be estimated using the coincidence Doppler broadening results. In order to calculate the defect density, it is needed to assume at least two types of defects. A parametric study has shown that the short lifetime traps have a lifetime component of about 160 ps.

These quantitative results have then been compared with other techniques, such as APT, SANS and TEM. It has been proven that the results coming from the PAS experiments are reliable, and the combination of the four techniques leads to a good comprehension of all defect populations created during irradiation.

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