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On the empirical determination of positron trapping coefficient at nano-scale helium bubbles in steels irradiated in spallation target

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ABSTRACT

In the present work, the specific positron trapping rate of small helium bubbles was empirically derived from positron annihilation lifetime spectroscopy (PALS) and transmission electron microscopy (TEM) studies of Fe9Cr martensitic steels. Both techniques are well known to be sensitive to nanometer-sized helium-filled cavities induced during irradiation in a mixed proton-neutron spectrum of spallation target. Complementary TEM and PALS studies show that positrons are being trapped to these defects at a rate of $1.2 \pm 0.8 \times 10^{-14}$ $m^3 s^{-1}$. This suggests that helium bubbles in ferritic/martensitic steels are attractive traps for positrons comparable to mono-vacancies and quantitative analysis of the bubbles by PALS technique is plausible.

1. Introduction

The development of new materials for nuclear applications is often confronted with the production of transmutation elements. A particularly challenging problem is the production of gasses such as helium and hydrogen. Helium is essentially insoluble in metals and strongly interacts with vacancies and forms bubbles at different sites [1]. Understanding its accumulation in materials is thus a fundamental scientific objective with significant practical implications.

As for the experimental investigation of the helium behaviour in irradiated materials, any characterization method used must be sensitive to sub-nm scale defects on one hand and to the light helium atoms on the other hand. Some experiments on TEM imaging in combination with electron energy loss spectroscopy (EELS) were reported providing qualitative data on nanometre-sized helium bubbles [2]. However, usually only a weak fingerprint of helium can be seen in the EELS spectrum. Moreover, this approach is limited by the TEM resolution to relatively large He bubbles >2 nm [3].

Positron annihilation spectroscopy (PAS) is known to be very sensitive to vacancy-type defects as small as mono-vacancies at concentrations as low as 0.1 appm [4]. Furthermore, the interaction of positrons with an open volume defect in a crystalline structure is strongly influenced by the presence of helium [5]. This makes positrons an ideal probe for the investigation of early-stage damage in irradiated materials.

The present work combines and complements experimental PAS data with TEM observations in order to provide a guideline for quantitative assessment of helium-vacancy agglomerations in the irradiated materials by means of positron annihilation lifetime spectroscopy (PALS).

2. Theoretical model

In our previous paper on the helium behaviour in ferritic/martensitic steels irradiated in a target of the Swiss Spallation Neutron Source (SINQ) [6] we used a three-component trapping model (Eq. (1)) to evaluate obtained lifetime spectra and to characterize two distinct categories of radiation-induced vacancy-type defects. Short defect component (with lifetime τ_2 and intensity I_2) was attributed to positron trapping at small helium-vacancy

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clusters (HVC). Long defect component (τ_3, I_3) was attributed to a trapping at TEM resolvable helium bubbles (HB). According to the trapping model, the annihilation rate $\lambda = 1/\tau$ is proportional to the local electron density at the site of the annihilation. Thus, the number of positrons, n_d, decays with time according to the linear combination of three exponentials:

$$n_d(t) = n_0 \sum_{i=1}^{3} I_i \exp\left(-\frac{t}{\tau_i}\right) \quad (1)$$

with n_0 being the number of positrons at time $t = 0$ and $I_1+I_2+I_3 = 1$.

While τ_2, I_2, τ_3, I_3 refer to vacancy-type defects, the lifetime and intensity (τ_1, I_1) describe the annihilation with delocalized (untrapped) positrons. The actual measured value of τ_1 is reduced from the theoretical bulk value $\tau_B = 1/\lambda_B$ due to the trapping at defects (Eq. (2)). The comparison of the calculated and the measured τ_1 values can be used to test the applicability of the decomposition. The discrepancy shall be < 5 ps [7].

$$\lambda_1 = \lambda_B + \kappa_1 + \kappa_2;\ I_1 = 1 - I_2 - I_3 \quad (2)$$

The (total) positron trapping rate at defects (per unit time) is given by the trapping rates κ_{HVC} and κ_{HB} that can be calculated from the experimental data and equations 3 and 4

$$\lambda 2 = \lambda_{HVC};\ I2 = \kappa_{HVC}/(\lambda_B - \lambda_{HVC} + \kappa_{HVC} + \kappa_{HB}) \quad (3)$$

$$\lambda 3 = \lambda_{HB};\ I3 = \kappa_{HB}/(\lambda_B - \lambda_{HB} + \kappa_{HVC} + \kappa_{HB}) \quad (4)$$

The rate of positron trapping at defect is proportional to the number density of the given defect, i.e.

$$\kappa_{HVC(HB)} = \mu_{HVC(HB)} N_{HVC(HB)} \quad (5)$$

The proportionality constant μ is called the specific trapping rate or trapping coefficient. Depending on whether atomic or volume defect concentration is considered, this coefficient is given in s^{-1} or $m^3 s^{-1}$ units, respectively. The conversion between these two units can be done using the formula

$$\mu\left[m^3 s^{-1}\right] = \frac{\left[s^{-1} at.\right]}{N_{at}\left[m^3\right]} \quad (6)$$

where N_{at} is the number of atoms in the unit volume. In this paper, we use $m^3 s^{-1}$ units [7].

At constant temperature, the specific trapping rate μ depends on the size of the vacancy cluster. A complementary view is that the cluster of vacancies can be considered as a positron potential well the depth of which is related to the size for a given type of defect. Like characteristic lifetimes, specific trapping rates are known for a number of defects. For instance, a positron lifetime of 175 ps and the corresponding specific trapping rate $1.1 \times 10^{15}\ s^{-1}$ ($1.3 \times 10^{-14}\ m^3 s^{-1}$ for $N_{at} = 8.49 \times 10^{28}\ m^{-3}$) have been reported in the literature for an empty mono-vacancy in iron [8]. For vacancy clusters, these values increase with the cluster size expressed by the number of vacancies in the cluster (n). The positron lifetime increases almost linearly with the number of vacancies in a small cluster up to ~20 vacancies [9]. The positron lifetime for clusters in metals with more than 30 vacancies saturates at 400–500ps and does not increase anymore with cluster size. As for μ, it has been found to be proportional to r^3 for small clusters, with r being their radius [10]. According to Nieminen and Laakkonen [11] we can assume that the specific trapping rate for a small vacancy cluster ($n \leq 10$) is proportional to n, which is compatible with the previous statement. Further in the paper, we use an example of a cluster of 10 vacancies ($\tau = 285$ ps) having a specific trapping rate $\mu_{10} = 10 \times \mu_1 = 1.3 \times 10^{-13}\ m^3\ s^{-1}$.

The situation is more complicated when these clusters contain helium. As can be seen in the work of Eldrup et al. on aluminium [12], the slope of the $\tau(n)$ dependence decreases with the helium content and it approaches zero when the He/V ratio = 2. Naturally, the saturation of the lifetime for large clusters decreases with helium density. The theoretical calculations [13] have yielded a numerical relationship between positron lifetime, τ (in units of ps), and He density, n_{He} (in units of $10^{28} m^{-3}$) inside bubbles in Al at room temperature:

$$\tau = 500 - 23.5 n_{He} \quad (7)$$

The dependence of the specific trapping rate at helium-vacancy clusters (bubbles) on the concentration of He is still not known at present. In the present work, we attempt to determine the value of this coefficient for small helium bubbles (1–1.8 nm) in ferritic/martensitic (F/M) steels. For this purpose, we used TEM analysis performed on the materials investigated by PALS.

3. Experimental

Two F/M steels, F82H and CLAM, irradiated in the Swiss spallation neutron source (SINQ) at the Paul Scherrer Institute (PSI) were investigated in the present work. The chemical composition of the both steels [14,15] is given in Table 1. Detailed irradiation parameters are given in Table 2.

In the case of the F82H steel, PALS measurements were performed on the grip section of large tensile samples after punching out of TEM samples [16]. For the CLAM steel, PALS was performed on different samples to the TEM analysis, but with a very similar dpa, irradiation temperature and transmutated helium content [17]. While the F82H samples were investigated using an external ^{22}Na positron source, in the case of the CLAM samples an internal $^{44}Ti/^{44}Sc$ source was used. The mean implantation depth of positrons in the first case is a few tens of micrometres, while in the latter case the positrons are produced homogeneously within the sample. In either case, the volume of the studied region is negligible compared to the gradient of irradiation parameters between two investigated spots [18]. All samples studied in the present work were irradiated near the peak of the proton and neutron flux, where ~60% of dpa is induced by protons and ~40% is induced by neutrons.

4. Results and discussion

The positron specific trapping rate was investigated for small helium bubbles (1–1.8 nm) in the two F/M steels. These defects are represented in the three-component decomposition of the lifetime

Table 1
Chemical composition of the F82H and CLAM steels (Fe in balance).

Material	Cr	Ni	Mo	Mn	V	W	C	Ta	Si	N	Other
F82H	7.87	0.02	0.003	0.1	0.19	1.98	0.09	0.03	0.07	0.007	<0.03
CLAM	8.91	–	–	0.49	0.2	1.44	0.12	0.15	0.11	–	–