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Vacancy-solute complexes and their clusters in iron

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Abstract

In this contribution, several vacancy-solute complexes in iron are investigated theoretically from the viewpoint of positron annihilation. In particular, V-Si, V-P, V-Cr, V-Mn, V-Ni, V-Cu and V-Mo complexes are examined. In addition, nano-sized vacancy-Cu clusters in the Fe matrix are also studied. We concentrate on positron lifetimes and coincidence Doppler broadening profiles that bring complementary information about the studied complexes and their clusters. Positron calculations are carried out using the atomic superposition method employing realistic atomic configurations obtained recently using an ab initio pseudopotential method (vacancy-solute complexes) and Monte Carlo/molecular dynamics methods (vacancy-Cu clusters). The main aim of this study is to predict as to what extent such defects are detectable and differentiable using positron annihilation techniques. The results obtained are discussed in the context of experimental data available in the literature.

Keywords: Vacancy-solute complexes; Vacancy-solute clusters; Electron–positron momentum distribution; RPV steels; Atomic superposition method

1. Introduction

Vacancy-solute complexes and their clusters play an important role in iron alloys (steels). Such defects appear in steels after irradiation and/or deformation,

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which affects macroscopic properties of exposed materials. This is certainly important for practical applications, e.g. for the nuclear industry where the mechanical properties of reactor pressure vessel (RPV) steels are of primary importance with respect to the operational safety of nuclear power plants. In particular, it is well known [1] that embrittlement of RPV steels is due to their hardening. Such hardening is caused by the matrix damage during irradiation and irradiation enhanced precipitation of Cu-rich nano-clusters that contain vacancies, too. Thus, both vacancy-solute complexes and Cu-vacancy clusters are of great importance in the embrittlement process and it is, therefore, desirable to study them in detail.

Positron annihilation spectroscopy (PAS) is well known to have unique sensitivity to open volume defects in materials [2] and is also capable of detecting atomic environment of positron annihilation (PA) sites [3]. Recently, various iron-based model alloys were studied experimentally by Nagai et al. [4] with the aim to identify vacancy-solute complexes in these alloys using PAS. The purpose of the present work is to provide quantitative tools for such identification by calculating the positron lifetimes and high momentum parts (HMPs) of coincidence Doppler broadening (CDB) spectra [3] corresponding to such complexes whose atomic configurations were determined by a first-principles pseudopotential technique.

Furthermore, Cu-vacancy clusters are known to be formed in Fe–Cu alloys upon neutron irradiation [5–7], deformation [8] and ion implantation [9]. These clusters have the form of vacancy clusters covered by Cu atoms [5]. Cu-rich 'clouds' or 'atmospheres' that could resemble clusters detected by PAS were also found using the tomographic atom probe and 3D atom probe. In order to give a quantitative description of such clusters in terms of their size and level of Cu coverage/coating, we calculated the dependence of the positron lifetime and the so-called *W*-parameter, which also reflects HMPs, on the Cu content for selected vacancy clusters obtained using a combination of Monte Carlo (MC) and molecular dynamics (MD) simulation techniques.

We should also note that the research presented here is a part of broader activities devoted to the investigation of model Fe-based alloys with the aim to provide reliable parameters for multiscale modeling of such alloys and RPV steels in general [10].

2. Computational methods

Recently, a computational study of selected vacancy-solute complexes in iron has been performed with the aim to find solution enthalpies, solute–solute and vacancy-solute binding energies, to evaluate the solute diffusion mechanism and to determine relaxed defect geometries [11]. The Vienna ab initio simulation package [12] was employed in these calculations. Within the frame of this package, a pseudopotential approach is used. All computational details together with the discussion of results can be found in ref. [11]. Here for the purpose of positron calculations, we employ relaxed defect configurations obtained using 54 atom supercells ($3 \times 3 \times 3$ bcc cell of Fe).

Furthermore, the atomic configurations of copper-vacancy clusters (CuVCs) have been obtained using MC and MD techniques [13]. In the first step, an MC technique is employed to find the lowest energy of the cell containing a defined CuVC (i.e. a cluster with a given number of vacancies and Cu atoms) considering the rigid lattice. In the second step, such a configuration is relaxed using the MD method. In these simulations, the empirical many-body potential for the Fe–Cu system derived by Ludwig et al. [14] was utilized. The whole description of the computational procedure and obtained results are given in ref. [13]. The primary goal of that study is to find CuVC atomic configurations together with their formation energy as well as binding energies of Cu atoms and vacancies in order to help understanding the process of the cluster formation in real materials.

Positron calculations were carried out employing the so-called atomic superposition (ATSUP) method [15]. In the case of vacancy-solute complexes, the 54 atom supercells were extended to 686 atom ones by adding Fe atoms at the sides of these supercells. Such added atoms were positioned on regular Fe bcc lattice sites. As for vacancy-Cu clusters in iron, the size of supercells varies from 1024 to 2000 atoms. The scheme described in ref. [16] was utilized for calculations of HMPs of the momentum distribution of annihilation photons (CDB profiles). The range $(15–25) \times 10^{-3} m_e c$ was considered in calculations of the *W*-parameter. Core electron configurations for all atomic species are specified in Table 1. In the case of atoms with d-electrons, it is often necessary to reduce the number of d-electrons considered in HMP

Table 1
Core electron configurations for Fe and studied vacancy-solute complexes: results of calculations of the positron lifetime (τ), W-parameter and positron binding energy to defects (E_b) for vacancy complexes and other examined defects

Complex	Core	τ (ps)	10 W	E_b (eV)
Bulk	(Ar) + $3d^6$	97	0.278	–
V	–	153	0.178	2.61
V_2 (1 nn)	–	173	0.150	4.09
V_2 (2 nn)	–	158	0.173	3.44
V-Si	(Ne)	152	0.167	2.48
V-P	(Ne)	153	0.163	2.66
V-Cu	(Ar) + $3d^{10}$	153	0.206	2.88
V-Cr	(Ar) + $3d^5$	154	0.177	2.60
V-Mn	(Ar) + $3d^5$	152	0.176	2.54
V-Ni	(Ar) + $3d^8$	154	0.184	2.77
V-Mo	(Kr) + $4d^5$	152	0.174	2.46

calculations to reproduce well the experimental CDB profiles (see e.g. [17]). Such a correction was neglected in the case of vacancy-solute clusters because we do not have available CDB profiles for all d-elements involved. As for CuVCs, we reduced the number of d-electrons to 2 and 3 for Fe and Cu atoms, respectively. The calculated spectra were convoluted with a Gaussian function with the width 1 keV (=$3.91 \times 10^{-3} m_e c$; full width at half maximum), which corresponds to a typical experimental energy resolution of CDB spectrometers. In the present work, the enhancement introduced by Stachowiak and Lach [18] was employed in lifetime and HMP calculations in order to ensure the proper behavior of the enhancement for larger vacancy clusters (i.e. small electron densities). We further refer to refs. [19,20] for details concerning theoretical approaches and related computational procedures used in positron solid-state physics.

3. Results and discussion

3.1. Vacancy-solute complexes

Table 1 contains results of the positron lifetime, W-parameter and positron binding energy calculations for the studied vacancy-solute complexes. In addition, we specify results for the bulk (defect free) Fe, single vacancy (V) and divacancy (V_2) in Fe. In the case of divacancy, the calculations [11] show that there is strong binding between two vacancies in the first nearest neighbor (1 nn) and second nearest neighbor (2 nn) configurations – the latter one having even a larger binding energy – and, therefore, we consider them both in positron calculations.

One can see that the used enhancement [18] underestimates somewhat both the bulk and single vacancy lifetimes. The experimental values are, respectively, 107 ps and 175 ps (see ref. [8] and references therein). This should be taken into account when comparing measured and calculated values. Furthermore, the divacancy in the 2 nn configuration behave almost as the single vacancy, which makes both defects probably unresolvable (this also applies to HMP profiles; see below). The lifetimes of the studied vacancy-solute complexes are all in the range 152–154 ps and, therefore, complexes are not differentiable using positron lifetime spectroscopy. The positron binding energy (E_b) does not exhibit a large variety among the studied defects, except for divacancies.

As for the W-parameter values, they show somewhat larger deviations from the single vacancy value compared to the lifetime and E_b. The largest deviation occurs for the V-Cu and V_2 (1 nn) defects; in a smaller extent also for V-P, V-Si and V-Ni complexes. This becomes even more apparent from the ratio HMP profiles plotted in Fig. 1. Indeed, the ratio profiles of V_2 (1 nn), V-P and V-Si defects (Fig. 1a) differ from that of the single vacancy and their mutual resolution can be expected under favorable conditions, in contrast to V_2 (2 nn) that cannot be probably resolved from V. Fig. 1b shows the ratio profiles for remaining complexes (the solute atom contains 3d or 4d electrons). The largest deviation from the profile of the single vacancy occurs for the V-Cu complex. The deviation for the V-Ni complex is apparently smaller. However, V-Cu and V-Ni complexes become unresolvable if they are both present in a sample. There is still a small chance to differentiate V and V-Mo defects due to the feature around $20 \times 10^{-3} m_e c$ present in the V-Mo ratio profile.

As mentioned above, Nagai et al. [4] studied several Fe-based model alloys with the aim to identify vacancy-solute complexes and their clusters. There is an indication of the existence of a V-Cu_n ($n \geq 6$)

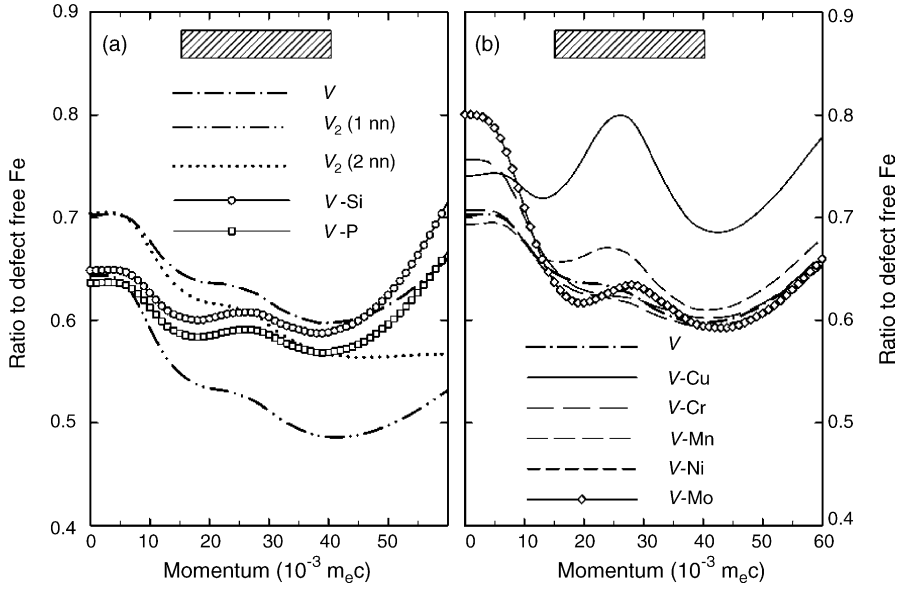

Fig. 1. Calculated HMP ratio profiles for the studied vacancy-solute complexes and vacancy-type defects in iron: (a) V, V_2 (1nn), V_2 (2nn), V-Si and V-P defects and (b) V, V-Cu, V-Cr, V-Mn, V-Ni and V-Mo. The shaded area indicates the momentum region that can be usually compared to experiment.

defect. Furthermore, Ni atoms bound to small vacancy clusters and C atoms bound to the single vacancies were also detected. However, the defect CDB (ratio) profiles were not extracted in ref. [4] and a direct comparison with profiles presented in this work is not possible. Thus, further experimental and computational effort is required in order to characterize better the vacancy-solute complexes and related defects in model alloys.

Finally, we would like to mention that a similar topic – vacancy-solute complexes in the Al matrix – was investigated in another article in these proceedings [21].

3.2. Copper-vacancy clusters

For positron calculations we selected vacancy clusters with 3, 9 and 25 vacancies. Figs. 2 and 3 summarize, respectively, the results of positron lifetime and *W*-parameter calculations. The right part of the figures shows dependencies of the quantities of interest on the number of Cu atoms in the cluster, i.e. dependencies on the Cu decoration/coverage. The left part of these figures contains the dependence of corresponding quantities on the size of vacancy clusters without any Cu decoration.

As indicated by Fig. 2, the positron lifetime almost does not depend on the level of the Cu coverage (except for small clusters) and this means that the positron lifetime can be used to estimate the size of the open volume of CuVCs in terms of the number of vacancies. On the other hand, Fig. 3 shows that the *W*-parameter depends obviously on the Cu coverage. Thus, according to the number of vacancies determined by the lifetime, the corresponding *W*-parameter curve can be chosen, and on the basis of the measured value of the *W*-parameter the Cu coverage can also be estimated. This is complicated by the fact that the dependencies in Fig. 3 are not perfectly smooth (especially for small number of vacancies), but we believe that in this way CuVCs in real samples can be characterized quantitatively with a definite degree of precision, which could enhance significantly the ability of PAS to explore such clusters.

CuVCs were also studied experimentally [5–9]. For instance, the positron lifetimes 300 ps and 280 ps given for CuVCs in refs. [5] and [8], respectively, for as-prepared samples correspond to clusters with about 10 and 8 vacancies. However, the *W*-parameter (if presented) is calculated in a different range than here, which does not allow for a direct comparison at this

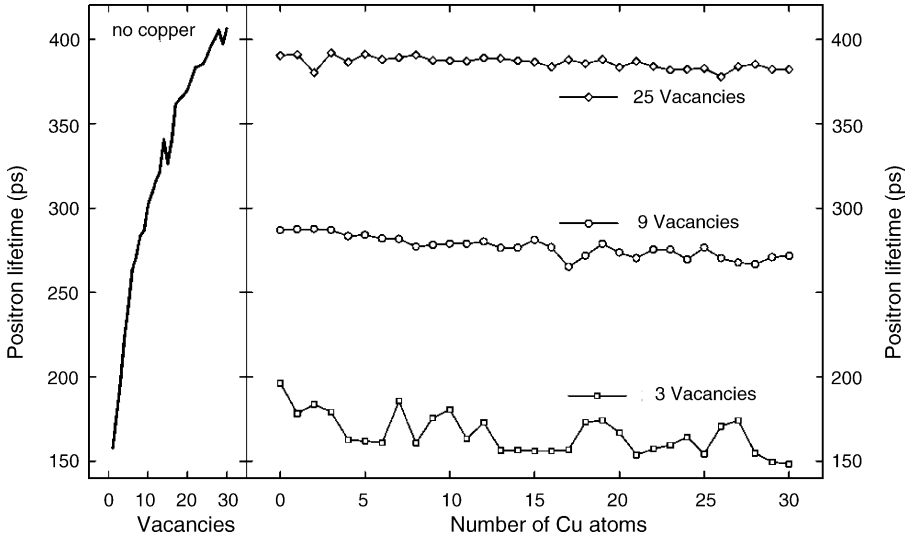

Fig. 2. The dependence of the positron lifetime on the vacancy cluster size (left panel) and on the copper coverage of selected vacancy clusters (right panel) (see the text for further explanations).

moment. Further work is in progress to analyze a larger amount of simulated atomic configurations of CuVCs and to compare experimentally found PA response with the calculated one in order to characterize quantitatively CuVCs existing in real samples. In addition, we intend to investigate to what extent PA response depends on the type of the empirical potential used for the simulations, as this appears to be related to the issue of complete Cu coverage/coating of vacancy clusters (see ref. [13] for details).

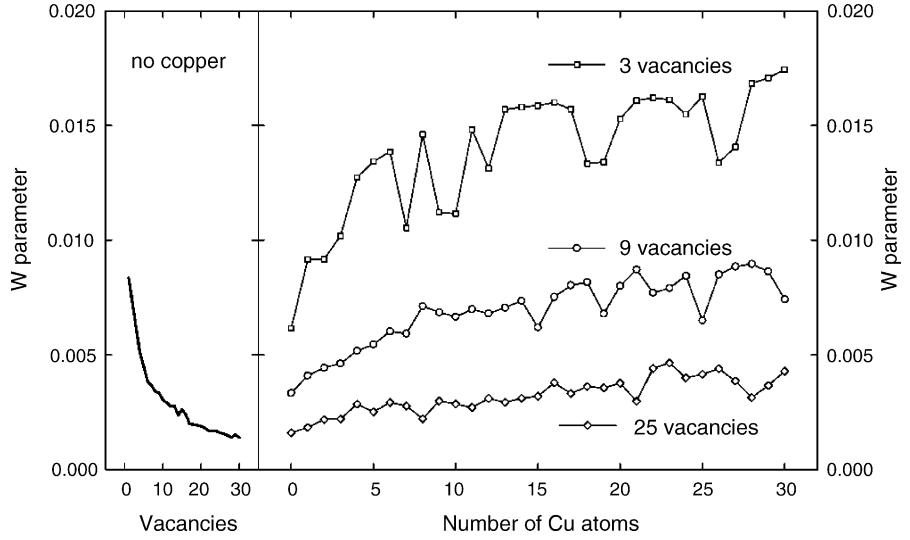

Fig. 3. The dependence of the *W*-parameter on the vacancy cluster size (left panel) and on the copper coverage of selected vacancy clusters (right panel) (see the text for further explanations).

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