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Journal of Nuclear Materials 359 (2006) 93–101
journal of nuclear materials
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Positron lifetime calculations of defects in chromium containing hydrogen or helium

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Received 6 October 2005; accepted 30 July 2006

Abstract

The characteristics of defects in chromium containing hydrogen or helium atoms have been investigated by positron lifetime quantum calculations. On the basis of calculated results, the behaviors of empty nano-voids and nano-voids with hydrogen or helium were discussed. It was found that hydrogen and helium in larger three-dimensional vacancy clusters change the annihilation characteristics dramatically. The hydrogen and helium atoms are trapped by lattice vacancies. Helium bound with vacancies can form larger size cluster in chromium. These results provide physical insight for positron interactions with defects in chromium and can be used for prediction of hydrogen or helium generation for the design of fission and fusion reactors. The positron lifetime calculations were performed by the standard DFT density functional theory method. The electron wave functions have been obtained in the local density approximation LDA to the DFT.

PACS: 78.70.Bj

1. Introduction

This paper is concerned with the study of defects in chromium. Chromium is a 3d metal of considerable interest due to its application in the advanced structural materials like Fe–Cr [1], Fe–Cr–Ni, 9Cr–1Mo steels [2]. Corrosion resistance, hydrogen storage capacity and exposure to the high-energy neutron irradiation are important characteristics for high temperature chromium applications. The 9CrWVTa – Reduced Activation Ferritic Martensitic RAFM steel called Eurofer is the reference structural material for the DEMO blanket. The results of alloys containing chromium pointed out differences in the defects in the alloy as to the pure chromium [2]. For comparison of the future results from model calculations of defects in new structural materials containing chromium, it is necessary to carry out also calculations of defects in pure chromium. The specific focus of this study is on the model calculations of positron lifetime of defects in chromium containing hydrogen or helium. Positron lifetime spectroscopy is a powerful and sensitive technique for studying defects with the

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0022-3115/$ - see front matter
doi:10.1016/j.jnucmat.2006.07.020

concentration as low as 10^{-6} [3] in metals. The method is based on the positron trapping at open volume defects. The positron trapping in pure metals may be used for characterization of mono-vacancies, divacancies and vacancy-clusters. The annihilation characteristics of a positron trapped at a vacancy or empty nano-voids are different from those of positrons trapped at nano-voids containing hydrogen or helium. This fact shows that the presence of hydrogen or helium in samples influences the behavior of defects in samples. The interaction of positrons with defects containing hydrogen or helium illustrates interesting physical concepts concerning hydrogen or helium trapping by vacancy clusters. Neutron irradiation creates atomic displacements and generates helium or hydrogen in samples by atomic transmutations. The production of hydrogen or helium in irradiated chromium is dependent on the following nuclear reactions: (n,α) and (n,p). An unavoidable by-product of spallation reactions is the formation of large amounts of hydrogen in the target material. The retention of hydrogen or helium in the first wall, determined by hydrogen-defect or helium defect interactions, influences the plasma parameters. At elevated temperatures point defects gather into clusters and the vacancies grow into the nano-voids. The properties of point defects in 14 MeV neutron irradiated chromium have been the subject of the paper of Troev et al. [4]. Chromium ($3d^5 4s^1$) has bcc lattice. The interaction between hydrogen or helium and defects in metals like Cr, W, V, Ni plays an important role in various areas of technology [2,5]. Chromium is a corrosion-resistant material. It absorbs a lot of hydrogen. The chromium alloys are good hydrogen storage materials. The major difficulties in investigating intrinsic defect properties in chromium after neutron irradiation originate from the hydrogen and helium interactions with vacancies and vacancy clusters. Hydrogen concentration as low as 10^{-5} atomic fraction causes serious mechanical changes [6,7]. High amount of helium ($\sim$1000 appm He) can be generated in all materials proposed for fusion reactor first wall applications in the lifetime of a fusion reactor [8]. Degradation of the mechanical properties increases with increasing of hydrogen or helium content. In a fusion reactor the first wall will be bombarded by D, T and He particles. Interstitial hydrogen has high mobility in metals [9,10]. The solubility of hydrogen in metals is usually small and it is known to increase in the presence of nano-voids. This is due to the trapping of hydrogen at these defects. The positron density profiles in a pure vacancy and vacancy–hydrogen or vacancy–helium complexes are very different [11].

In this work, by using quantum-mechanical electronic-structure calculations based on the DFT, the positron lifetime characteristics have been applied to clarify the behavior of vacancy-type defects containing hydrogen or helium atoms in chromium. The main emphasis has been put on the investigation of empty nano-voids and nano-voids with different hydrogen or helium concentrations. The determination of positron lifetimes for various defects in chromium has not been completely performed yet both in the experiments and in the model calculations. The aim of the computer model calculations for chromium is to obtain the electron and positron wave functions and the corresponding eigenvalues of energy. As pointed out in the paper [12] the large void can be considered as an internal surface. It is founded that He atoms tended to cluster together to form helium bubbles. The helium bubbles had large binding energies with vacancies. In the computer calculations a system of 800 atoms in a cell is typically sufficient to obtain accurate results for positron lifetime and positron ground state energy for the largest nano-void containing 6 V and 6 He atoms. The results from calculations with more than 2000 atoms in cubic cell were identical each-other within 0.01 eV for the total crystal lattice energy.

2. DFT positron lifetime computation method

Based on the DFT we performed positron lifetime calculations of vacancy-clusters, using the Kohn–Sham approach [13]. The positron trapping is influenced by a lowered annihilation rate, due to the lower electron density. Our calculation model can handle several thousands of Cr atoms in a bcc lattice. We have used 2000 atoms in a cubic cell with periodic boundary conditions. The time step was 0.0025 ps, the equilibration process was 5 ps and the calculation of positron lifetimes was made after another 40 ps. The number of electrons in chromium is so large that the calculation could be treated using statistical arguments. According to DFT the correct ground-state energy of an interacting electron gas in an external potential can be determined by minimizing the functional of the electron density. That is why we do not need the full wave function but only the electron density. In order to understand the effect of hydrogen and helium bound with vacancies on the positron lifetime, DFT calculations have been carried out as a

function of the vacancy-cluster size in chromium and the size of vacancy-clusters in chromium containing hydrogen or helium. The computed positron lifetimes could be also used to interpret the available experimental positron annihilation spectroscopy results for the nano-void size. The DFT calculations for Cr have been done with linear combination of Gaussian-type orbitals (LCGTO) based on the Kohn–Sham, LDA and Hohenberg–Kohn density-functional formalism in which the ground state property is a function of the electron density in position space [13,14]. The lattice constant for Cr is 0.288 nm while the distance between the bulk nearest-neighbours is 0.249 nm. The basis sets LCGTO are presented in Refs. [15,16]. The hydrogen and helium electrons are considered as valence electrons. The coordinate $z = 0$ corresponds to the starting point of the positron penetration through the (1 1 1) face of the Cr bcc structure for vacancy clusters in chromium and for clusters containing H. In the model calculations, the single H atoms are situated on a threefold site, which is located on the bulk tetrahedral interstitial site or on the octahedral interstitial site. The ratio of hydrogen or helium atoms versus vacancy sites in nano-voids has been varied. The positions of the atoms were allowed to relax to a minimum energy configuration. The relaxed lattice configuration is obtained through the iteration of the Newton–Raphson method. This iteration process is continued until the total energy of the chromium lattice reaches a saturated minimum value. The lattice relaxations for empty nano-voids and nano-voids with hydrogen or helium in chromium have been taken into account. Our results from positron lifetime calculations in Cr when lattice relaxation is included are shown in Figs. 3–8. The lattice relaxation around a vacancy results in about 9% reduction of the effective vacancy volume, causing decrease of positron lifetime at a vacancy. The vacancies were introduced by a modification of the BUBSIMUL algorithm [17]. In the density functional formalism [13,14] proposed by Hohenberg, Kohn and Sham the ground-state energy of an interacting electron gas is a function of the electron density $n(r)$. In the variational principle the electron wave function satisfies the following equations:

$$\begin{aligned} &\{-\nabla^2 + V_{\text{eff}}[n(r), r]\}\varphi_i(r) = \varepsilon_i\varphi_i(r), \\ &n(r) = \sum_i |\varphi_i(r)|^2, \\ &V_{\text{eff}}[n(r), r] = \phi(r) + V_{\text{xc}}[n(r)], \end{aligned} \tag{1}$$

where ε_i and φ_i are the eigenvalues and wave function, respectively, $n(r)$ is the electron density at the position r, V_{eff} is the effective potential experienced by the electron and $\phi(r)$ is the electrostatic potential derived from Poisson's equation.

$$\nabla^2\phi = -4\pi[n(r) - n_{\text{ext}}(r)], \tag{2}$$

where $n_{\text{ext}}(r)$ is the positive-charge density distribution. When the changes of $n(r)$ in the volume are small enough, we get a satisfactory result using the LDA [13,14]:

$$E_{\text{xc}}[n(r)] = \int n(r)\varepsilon_{\text{xc}}[n(r)]\,\mathrm{d}r, \tag{3}$$

where $\varepsilon_{\text{xc}}[n(r)]$ is the exchange correlation energy per particle in a homogeneous electron gas of density $n(r)$. The electronic structure of the point-like defect is obtained from the self-consistent solution of Eq. (1). $V_{\text{xc}}[n(r)]$ in Eq. (1) is the exchange correlation potential which is the derivative of the exchange correlation energy $E_{\text{xc}}[n(r)]$ with respect to the electron density $n(r)$.The single-electron Schrödinger equation entering in LDA is solved in the framework of the LCGTO method [16]. The positron wave function of the defect system is obtained by a method similar to that for electrons established by Puska and Nieminen [18], which satisfies the Schrödinger equation. To solve the Schrödinger equation the numerical method given by Kimball and Shortley [19] was used.

$$\{-\nabla^2 + V_+[n(r), r]\}\varphi_+(r) = \varepsilon_+\varphi_+(r), \tag{4}$$

where ε_+ and $\varphi_+(r)$ are the positron eigenvalues and positron wave function, respectively. V_+ is the positron potential. The energy eigenvalue of the positron wave function $\varphi_+(r)$ is obtained in each iteration. This process continued until the eigenvalue reaches a saturated minimum value. The positron lifetime is obtained by the wave functions and energy eigenvalues of the electron and positron in the defect system. The annihilation rate λ or the lifetime τ of a positron in an inhomogeneous electron gas is:

$$\frac{1}{\tau} = \lambda = \int \mathrm{d}r|\varphi_+(r)|^2\Gamma[n(r)], \tag{5}$$

where $\Gamma[n(r)]$ corresponds to the enhancement factor of electron density, due to the correlation between a positron and electrons. If the positron wave function is a planar wave function

$$\frac{1}{\tau} = \lambda = \Gamma[n_0] \int \mathrm{d}r |\varphi_+(r)|^2 = \Gamma(n_0). \quad (6)$$

Γ is composed of two electron densities (for valence electrons and for core electrons)

$$\Gamma[n(r)] = \Gamma_{\mathrm{v}}[n_{\mathrm{v}}(r)] + \Gamma_{\mathrm{in}}[n_{\mathrm{in}}(r)], \quad (7)$$

where $n_{\mathrm{v}}(r)$ is the valence electron density and $n_{\mathrm{in}}(r)$ is the core electron density [18].

3. Results and discussion

In Fig. 1(a) and (b) are shown the isometric plot and corresponding contour plot of the calculated positron density distribution PDD in an empty mono-vacancy in chromium. It is evident that positron is localized at the center of the mono-vacancy as shown in Fig. 1(a) and (b). The positron lifetime calculations have been performed in bcc Cr lattice

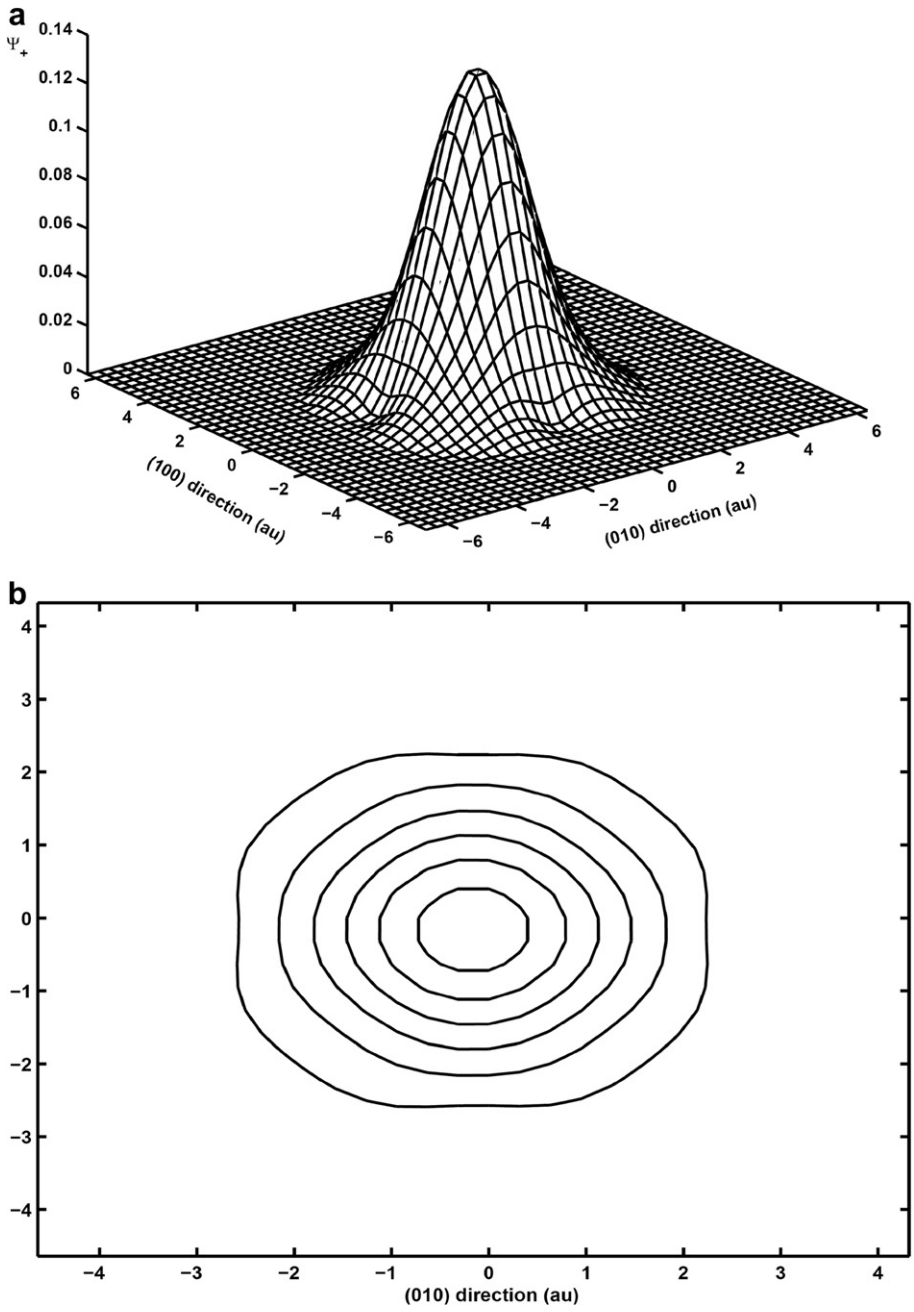

Fig. 1. Calculated localized positron wave function in bcc Cr vacancy: (a) isometric plot and (b) contour plot.

containing vacancies, empty nano-voids and nano-voids consisting from 1 to 6 vacancies with 1 to 10 hydrogen or helium atoms. Positron lifetimes have been also computed for nH-mV and nHe-mV clusters with different ratio ($n\langle\rangle m$), where n and m are the number of introduced hydrogen or helium atoms and vacancies number, respectively. The lifetime of a trapped positron is larger than that of the positron annihilating in the free state, because the density of electrons inside a vacancy is less than that in the interstitial region. The lifetime of a trapped positron is sensitive to the defect size as well as to the ratio of H to vacancies, or He to vacancies in nano-voids. In Fig. 2(a) and (b) are shown the

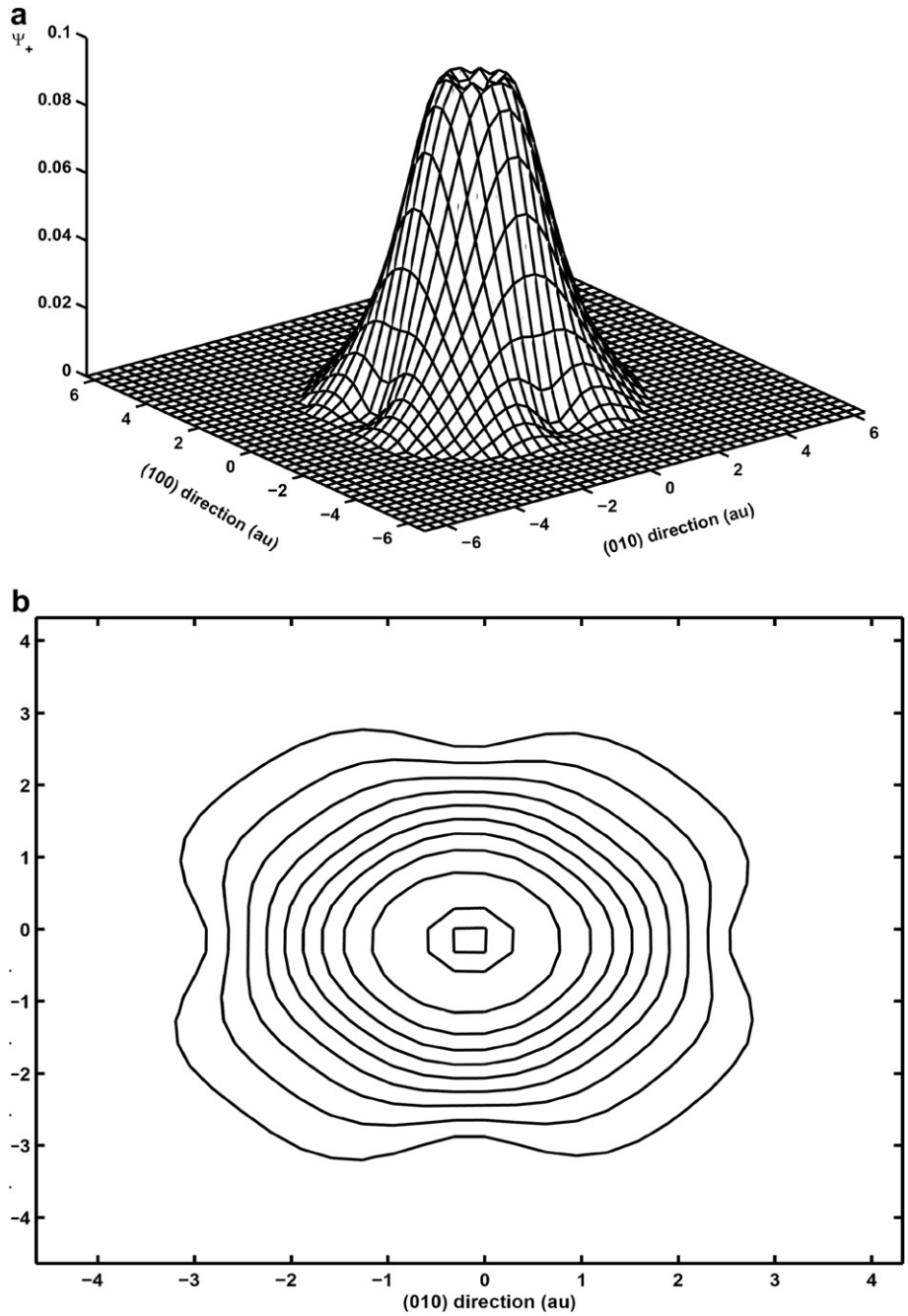

Fig. 2. Calculated localized wave function of a positron trapped in a mono-vacancy bound with one hydrogen atom in chromium (1V + 1H): (a) isometric plot and (b) contour plot.

isometric plot and the corresponding contour plot for the computed PDD in a chromium mono-vacancy with hydrogen. For a vacancy bound with an H atom, Fig. 2(a) and (b) – the isometric and contour plot of the computed PDD shows that a central hole appears in the PDD. This can be explained by the presence of the H atoms around the center of the void resulting in the exclusion of the positron from the center of the complex. The computed positron lifetime for a mono-vacancy 1V in chromium is 198 ps and for 1V–1H is 154 ps, respectively. We wish to point out that in the present work the relaxation calculations for lattice atoms have been performed to obtain the energetically most 'stable' configuration. At the beginning of the computation the inclusion atoms are located at the center of the created vacancy complexes nH/1V. The relaxation of the nH/mV is computed, while coordinates of the lattice 'border' peripheral atoms are not fixed – similar to the procedure in paper [20]. The H atom can 'diffuse' between Cr atoms, but we do not take into account the diffusion process. A correlation between the size of nano-voids containing hydrogen or helium and computed positron lifetime is established. For a hydrogen-vacancy 1V–1H the computed lifetime is 172 ps without lattice relaxation and 154 ps with relaxation of lattice atoms close to the defect. In both cases the positron lifetimes are lower than that of the pure Cr vacancy. In the hydrogen case when relaxation is considered, the electron density distribution is spread not in the center of the hole but at the vacancy border, while PDD is predominantly at the center of the vacancy. This explains the computed longer positron lifetime value. The calculated value of the positron lifetime in chromium is supported by the experimental value reported earlier in the literature [4]. The computed positron lifetime in chromium matrix without vacancy has a value of 103 ps, the experimental ones is 108 ps [4]. Both values are in good agreement. Our calculations show that positron in chromium is bound to the open defects even it contains a hydrogen atom. The lifetime of positrons in voids is longer than that for mono-vacancies and gives information for presence of vacancy-cluster with two or more vacancies. The variation of the calculated positron lifetime τ as a function of the vacancy-cluster size is shown in Fig. 3. A correlation between the vacancy cluster size and positron lifetime is established. Positron lifetime in chromium increases and tends to saturate around the values of 350 ps for nano-voids containing 14 vacancies. The longer lifetime corresponds to three-dimensional vacancy-clusters, namely, nano-voids, which are observed in bcc and fcc metal lattices, like Ni, Fe and Mo. The saturation typically occurs when the empty void radius reaches a value of about 1.0 nm. The computed positron lifetimes for a mono-vacancy containing hydrogen or helium in Cr are shown in Fig. 4, which presents the evolution of the complex of one vacancy bound with different number of hydrogen or helium atoms. The obtained results indicate the influence of the hydrogen or helium in the voids. Binding of hydrogen atoms with vacancies in chromium decreases positron lifetime because the introduced electron density by hydrogen led to increasing of the valence electron density. The positron lifetime decreases from 198 ps to 154 ps when one hydrogen atom is introduced into a mono-vacancy. It is seen that the values of calculated positron lifetimes decrease with increase of the number of hydrogen atoms. Positron lifetime

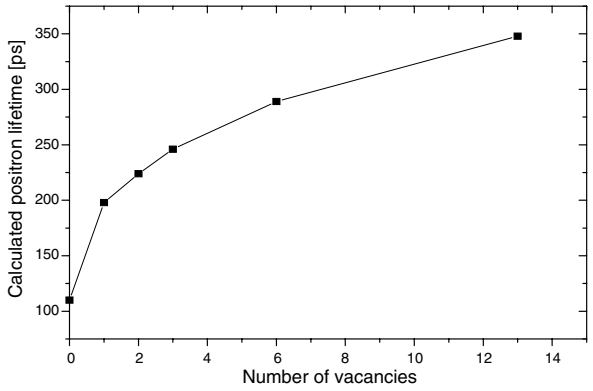

Fig. 3. Correlation between positron lifetime and the number of vacancies in the nano-void.

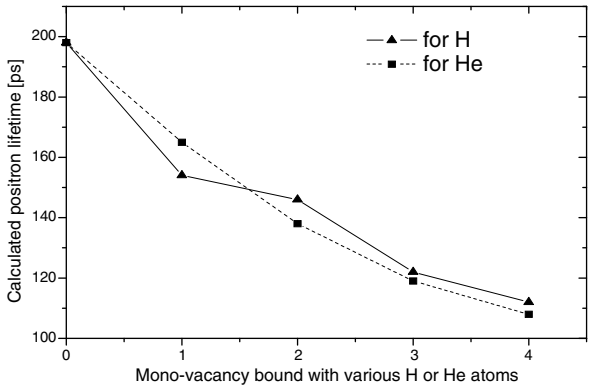

Fig. 4. Calculated positron lifetime as a function of hydrogen or helium atoms bound with mono-vacancy in Cr. (▲) for H; (■) for He.

decreases to 154 ps, 146 ps, 122 ps and 112 ps for a vacancy with one, two, three and four hydrogen atoms, respectively. For helium the calculated positron lifetime decreases to 165 ps, 139 ps, 121 ps and 110 ps. Our results also show a difference in the shape of the lifetime plot for vacancy-clusters containing H and the lifetime plot for He. The decrease in positron life time suggests an increase in H or He density inside of the nano-voids. Comparing the mean lifetime for vacancy with H or He to that of empty vacancy in Cr shows that the calculated values of the lifetime differ each other. This result for the first time indicates that the presence of single H or He atoms bound with mono-vacancy, affects the clustering of vacancies in chromium. Conversely, an increase in electron density due to the hydrogen or helium leads to an attractive site for positrons. In Figs. 4–6 is seen that with the growth of the number of vacancies the difference in the positron lifetime for H/He bound with vacancies becomes more significant due to the increasing number of electrons taking part in the cluster complex. The computed positron lifetimes are sensitive to the lattice relaxation for hydrogen or helium vacancy-clusters. The computed data for the case of multiple H atoms bound with a mono-vacancy and the multiple vacancies i.e. the ratio nH/mV is varied only by the inclusion of H atoms (n is varied, $m = \text{const}$,). It is interesting to note that our results show a sensitivity of the positron lifetime to the relative number of the hydrogen or helium atoms to the vacancies in the cluster. The computed positron lifetimes for corresponding vacancy-clusters containing hydrogen and helium are shown in Fig. 5 for 2V + mH and 2V + mHe atoms. The results indicate the influence of the added multiple H or He atoms in the voids on the positron lifetime. The computed lifetimes from introduction of H or He atoms in chromium voids show constant decrease. In Jellium-model [21] where the configuration of the defect complex is 'ignored', the calculated positron lifetime shows a monotonous decrease with addition of the hydrogen or helium atoms. In Fig. 6 are shown the results for the ratio nH/6V and nHe/6V. The positron lifetime decreases monotonously depending on the inserted hydrogen or helium atoms in the vacancy-cluster in chromium. The electron density of vacancy cluster remains lower than that of pure Cr sample and the values of the positron lifetimes are higher than that of chromium without vacancies. The obtained values from computed positron lifetime for six vacancies cluster in Cr containing 10H or 10He atoms is around 150 ps for 6V + 10H and 165 ps for 6V + 10He atoms, respectively. Increasing of hydrogen and helium concentration in the vacancy cluster leads to decrease of positron lifetime. The model calculations of vacancy clusters containing He show that the results are similar to the ones calculated for cluster containing hydrogen, the differences are in the values of the positron lifetime.

In Fig. 7 the calculated positron ground state energy and positron lifetime for various defects and voids containing hydrogen in chromium are summarized. It is observed that with increase of nano-void size 2V, 3V, 6V, 13V positron lifetime has higher values. It is interesting to note that the calculated values of positron ground state energy for nano-voids containing hydrogen are higher

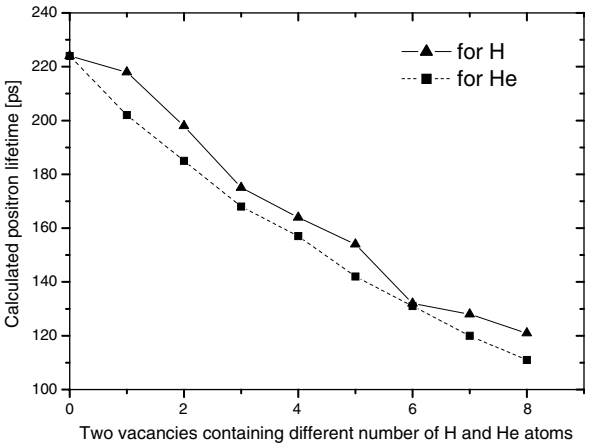

Fig. 5. Correlation between positron lifetime and the number of hydrogen or helium atoms in nano-void containing two-vacancies. (▲) for H; (■) for He.

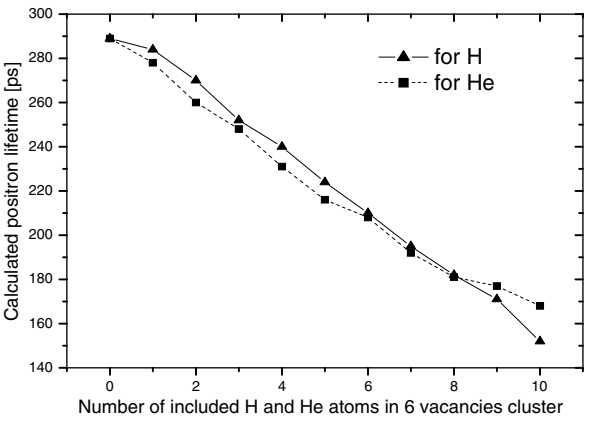

Fig. 6. Calculated positron lifetime in nano-void containing 6-vacancies and various H or He atoms. (▲) for H; (■) for He.

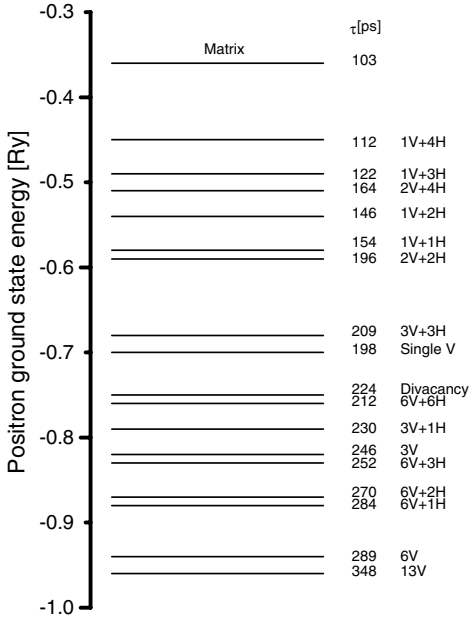

Fig. 7. Calculated values of positron ground state energy and positron lifetime for various defects in Cr; mono-vacancy, divacancy, empty nano-voids, nano-voids containing hydrogen atoms.

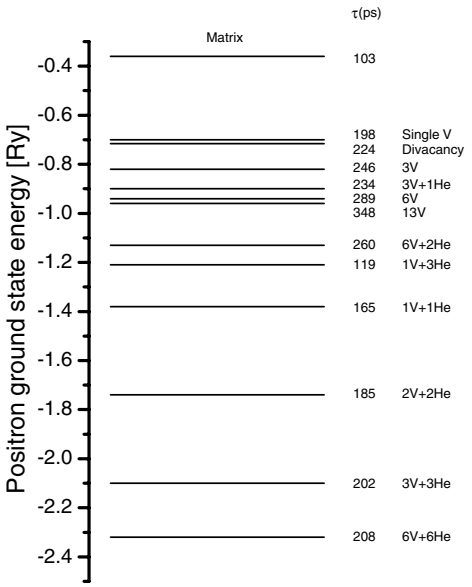

Fig. 8. Calculated values of positron ground state energy and positron lifetime for various defects in Cr; mono-vacancy, divacancy, empty nano-voids, nano-voids containing helium atoms.

than the corresponding values of pure (empty) nano-voids in chromium. The calculated values of the positron lifetime for nano-voids containing hydrogen are shorter than the corresponding values of nano-voids without hydrogen.

In Fig. 8 are presented the calculated positron ground state energy and positron lifetime results for vacancies, vacancy-clusters and vacancy-clusters containing different number of helium atoms. For small nano-voids e.g. containing less than 12 vacancies the calculated positron lifetimes give values in the range of 246–289 ps for V_3–V_6. The calculated values of the positron lifetime in chromium for nano-voids containing helium are shorter than the corresponding values of nano-voids without helium, while the calculated values of positron ground state energy for nano-voids containing helium are lower than the corresponding values of pure (empty) nano-voids. We consider that positron wave function is localized at the inner space of the nano-void. When the nano-void contains hydrogen or helium atoms the positron wave function is localized not at the center of the nano-voids, which gives a lifetime of the order of 209–212 ps for 3V + 3H and 202–208 ps for 3V + 3He atoms, respectively.

4. Conclusion

This positron model calculation study sheds light on the nano-defects formation and their evaluation in chromium containing hydrogen or helium. It is found that a positron is bound to a metal mono-vacancy even if it contains a hydrogen or helium atom. The model calculated positron lifetime for a nano-void with hydrogen or helium atoms is shorter than that for an empty nano-void of the same size, because the electrons from the center of the void attract positrons. The vacancy-cluster defects in chromium without helium or hydrogen are active positron traps, if once they are bound with He or H, they become less effective in the trapping of positrons. The calculated values of positron ground state energy for nano-voids containing hydrogen are higher than the corresponding values of pure (empty) nano-voids, while the calculated values of positron ground state energy for nano-voids containing helium are lower than the values of empty nano-voids. The DFT calculation of positron lifetime and positron ground state energy for vacancies and nano-voids containing hydrogen or helium leads to interesting practical applications since hydrogen, helium, empty voids and voids containing hydrogen or helium are expected to have different diffusive properties in chromium.

Acknowledgements

This research is done according to the Memorandum for Cooperation between the Institute for Nuclear Research and Nuclear Energy of the Bulgarian Academy of Sciences and Research Reactor Institute, Kyoto University, Japan. This work was partly supported by the Bulgarian National Research Council under contract F-903. Helpful discussions with Dr Shivachev are gratefully acknowledged.

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