Раздел первый

ФИЗИКА РАДИАЦИОННЫХ ПОВРЕЖДЕНИЙ И ЯВЛЕНИЙ В ТВЕРДЫХ ТЕЛАХ

UDC 539.4.015.1

DETERMINATION OF THE ENERGY OF SOLUTION OF A HELIUM ATOM AT GRAIN BOUNDARIES OF GENERAL TYPE

T.I. Mazilova, E.V. Sadanov, V.N. Voyevodin, O.V. Dudka, A.A. Mazilov, I.M. Mikhailovskij
National Science Center "Kharkov Institute of Physics and Technology",
Kharkov, Ukraine
E-mail: mikhailovskij@kipt.kharkov.ua

The relation between the potential energy of grain boundaries of general type and the value of dilatation of grain boundaries was determined by method of mathematical modeling in reciprocal space in tungsten. It is shown, that the electron density at the center of grain boundaries depended on the equilibrium grain boundary dilatation and the atomic density on boundary plane. The energy of solution of helium atom at the different twist boundaries of general type was obtained.

INTRODUCTION

Helium is an unavoidable by-product of the irradiation of reactor materials with energetic neutrons. The neutron irradiation in the fusion reaction encourages helium production by nuclear transmutation and defects creation in the first-wall material [1]. In fusion reactor devices, helium may accumulate at a rate of several hundred atomic parts per million per year. Accumulation of helium in metals in the form of the inert lattice gas, leads to their "helium swelling" and embrittlement. Tungsten is regarded as a potential plasma facing material in the future nuclear fusion reactors including both first wall and divertor plate because of its low sputtering erosion and high melting temperature [2, 3]. Facing materials suffer heavily bombardment of helium atoms and ions with energies from few tens of eV to several keV. Chemical inertia determines the helium behavior in the irradiated structural materials of nuclear reactors, where He is formed in substantial amounts due to nuclear fission reactions. Helium atoms play an important role in the microstructural response of tungsten to irradiation. Helium segregation at grain boundaries (GBs) results substantial embrittlement at low temperatures [2-4].

Helium is an insoluble inert gas typically produced to levels of a few tenths appm/dpa in fast reactor irradiations and to levels of up to tens of appm/dpa in fusion reactor environments. Formed helium atoms rapidly diffuse through the crystal lattice. The energy of solution of helium atoms in solids is large and, because helium does not form chemical composites with its host, it tends to accumulate at pre-existing or radiation-induced crystal defects, first of all, grain boundaries and vacancies, creating substitutional He atoms. Ab-initio calculations of energies of various He defect configurations showed that the energy of solution of a helium atom in metals is about or exceeds the formation energy of a self-interstitial atom. The calculated binding energy of a He-V complex for tungsten is 4,77 eV [2]. The aim of such researches is to develop an understanding of the mechanisms by which helium atoms alter physical and mechanical properties of metals. While up to now microstructural characterization forms a large part of this effort, development of a fundamental understanding of mechanisms is the major pursuit. An integrated theoretical and experimental approach is brought to bear on major problem areas. The grain structure can be destabilized if the stored energy associated with helium atoms accumulated at boundaries becomes greater than the energy required to make all the boundaries become free surfaces. In this case the grain boundaries split apart and the material fails. The energy of solution of a helium atom at grain boundaries is usually approximated by the energy of solution for a helium atom at a substitutional position in an ideal crystal lattice [2].

While the energy of solution of helium atoms was calculated for different atomic configurations in a perfect lattice for many metals [2], there are no theoretical calculations or experimental determinations of the solution energy of a helium atom at GBs. In the research that is reported here, we determined the energy of solution of a helium atom at GBs of general type [5, 6] in bcc-W using the reciprocal-space variational method [7, 8].

METHODOLOGY

The details pertaining to the methodology used in calculating the atomic structure and energetics of grain boundaries have been described elsewhere [6-8] and only an outline of the methodology is provided here. The Gerasimenko et al [9] method was used to determine local electron charge density due to surrounding atoms at the grain boundaries. The method involves calculating the energy of the atomic block as a function of lattice displacements for a particular wave vector.

Since mathematical simulations of GBs almost always employ periodic boundary conditions, it is very complicated to model incommensurate (general) boundaries, or GB of general type [5]. These GBs were

approximated by special boundaries with long periods. While many atomic simulations of GB failure have been performed, they have usually been confined to special boundaries with a high degree of symmetry. In this paper atomistic computer simulations were performed using molecular statics with conventional Morse potential. The thickness of the grain boundary interface model is taken as 31…40 atomic layers. This thickness is more than ten times larger than the range of the interatomic potential (0,65 nm) corresponding to 1,6 % of the well-depth for the Morse potential. Due to the homogeneous tensile force and the symmetry of the used cell, all the shear stress components were negligible. Constraints are placed on atoms located on these boundaries to stipulate that these interfaces remain planar and parallel during energy minimization. In this test, the tensile deformation was introduced by incrementally stretching the bicrystal in GB region a bit along the normal to the GB. These calculations correspond to local tensile destabilization due to the stored energy associated with helium atoms accumulated at boundaries at zero temperature.

The analysis of the interaction between planar atomic nets includes analytical determination of the Fourier transform of the potential. In such an analytical treatment has no need to limit the range of the pair potential by forcing it to vanish at relatively small separations. To obtain an analytical expression for the energy of interface, the effective pair potential was used in form

$$v(r) = \sum_p D_p \exp(-\beta_p r), \quad (1)$$

where r is the distance between atoms, D_p and β_p are adjustable parameters. The potential parameters were corresponding to the parameters of the classical Morse potential for tungsten [8].

It is assumed that the energy of the bicrystal is represented by a sum of pair interactions of atoms in j and k planar atomic layers. The lattice sites in these planes are denoted by the sets $\{\vec{X}^j\}$ and $\{\vec{X}^k\}$ and corresponding sets of the reciprocal lattice vectors are $\{\vec{G}^j\}$ and $\{\vec{G}^k\}$. The energy of interaction between two rigid parallel atomic layers per unit area is expressed as follows:

$$E_{jk} = \frac{1}{A_j A_k} \sum_{\vec{G}^c} \tilde{v}(\vec{G}^c, z_{jk}) \exp(i\vec{G}^c \cdot \vec{T}_{jk}), \quad (2)$$

where A_j and A_k are the areas of the primitive unit cells, z_{jk} is the separation between the lattices, $\vec{G}^c$ is a common reciprocal lattice vector, $\vec{T}_{jk}$ denotes an arbitrary relative translation, $\tilde{v}$ is two-dimensional Fourier transform of the pair-wise potential:

$$\tilde{v}(G, z_{jk}) = 2\pi \sum_p \frac{\beta_p D_p}{(\beta_p^2 + G^2)^{3/2}} (1 + z_{jk}\sqrt{\beta_p^2 + G^2}) \exp(-z_{jk}\sqrt{\beta_p^2 + G^2}). \quad (3)$$

In order to compute the total energy of the pair-wise atomic interaction W a lattice summation was performed. Within each plane parallel to the grain boundary we use the orthogonal coordinate systems x-y. The lattice periods in the x and y directions are α_x, α_y and $|\vec{G}| = \sqrt{g_{xl}^2 + g_{ym}^2}$ where $g_{xl} = \frac{2\pi l}{a_x}$, $g_{ym} = \frac{2\pi m}{a_y}$ and l, m are summation indices locating points in the planar reciprocal lattice. Here a – is the parameter of three-dimensional lattice. The module of the relative translation may be expressed as $|\vec{T}_{jk}| = \sqrt{T_{xjk}^2 + T_{yjk}^2}$.

Combining (2) and (3), we have

$$W = \pi\sigma^2 \sum_j \sum_{k(\neq j)} \sum_{lm} \sum_p \frac{\beta_p D_p}{q_{plm}^3} (1 + q_{plm}|z_{jk}|) \exp(-q_{plm}|z_{jk}|) \cos(g_{xl} T_{xjk}) \cos(g_{ym} T_{yjk}), \quad (4)$$

where $q_{plm} = \sqrt{\beta_p^2 + g_{xl}^2 + g_{ym}^2}$ and σ is the planar atomic density.

In our computer modelling the position of the rigid atomic planes have been labelled from $-20 < j,k < 20$. GBs of general type were produced by a rotation of grains about low-indices directions. The random (incommensurate) boundary can be obtained by a reducing the sets $\{\vec{G}^j\}$ and $\{\vec{G}^k\}$ to $G^j = G^k = 0$ ($l = m = 0$). The grain boundary dilatations were the main parameters determining the local electron density and helium energetic in the GB regions.

RESULTS AND DISCUSSION

Grain-boundary energetics are fundamentally described by the relation between the potential energy and an appropriate intergrain separation (grain-boundary dilatation). Such energy-distance correlation cannot be acquired for GBs with use of recent experimental techniques. In this paper GBs of general type were constructed using the reciprocal-space method [6-8] by a rotation of grains about low-indices directions by the angle corresponding to $\sum \to \infty$. As a result the twist GBs of general type oriented along the (100), (110), (111), and (211) crystallographic planes were acquired.

In Fig. 1 the grain-boundary binding energies as a function of separation of grains parting by the GB of general type with $\sum \to \infty$, where $\sum$ is the reciprocal density of coincident sites [5]. It is apparent that there are considerable variations in shape and depth of these curves and grain-boundary dilatations l corresponding to the energy minimums.

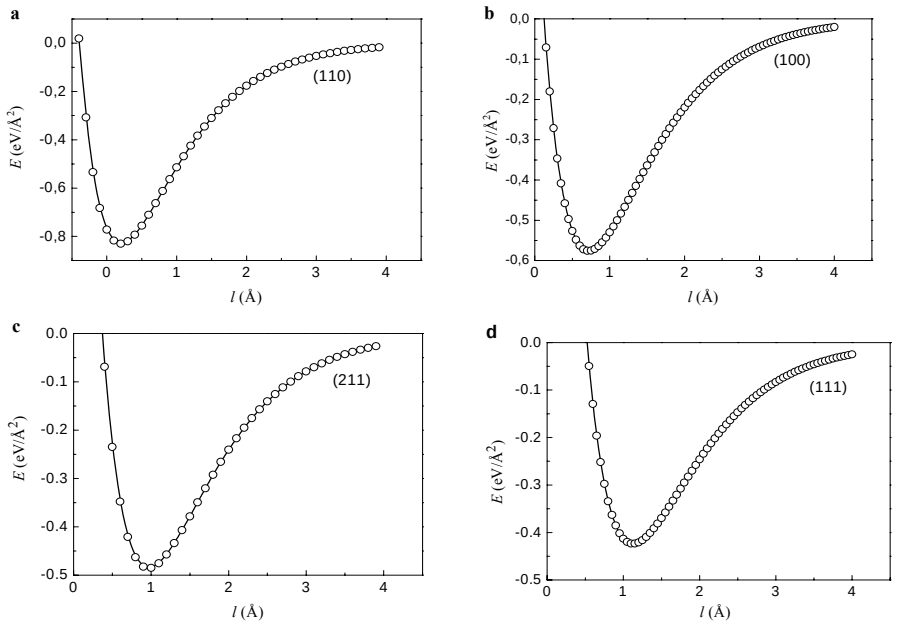

Fig. 1. Grain-boundary binding energy for tungsten vs the separation of grains on the twist grain boundaries of general type

Fig. 2 shows the dependence of the equilibrium GB dilatation *l* on the GB atomic density. The GB dilatation monotonically decreased with increasing of the GB atomic density.

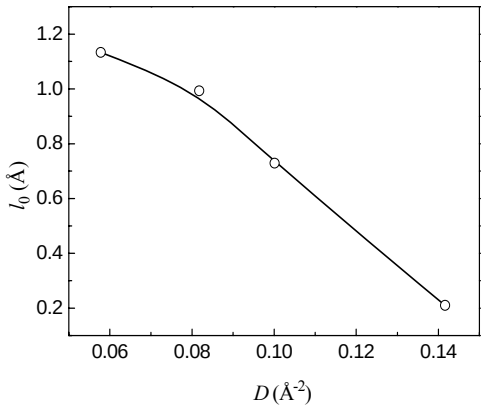

Fig. 2. Dependence of the equilibrium grain-boundary dilatation l on the GB atomic density for the low-index grain boundaries

Let us introduce a GB between two grains in the form of a gap in a homogeneous positive background (Fig. 3). The helium atoms are uniformly distributed in the plane z = *l*/2.

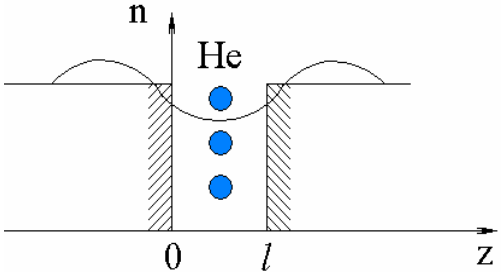

Fig. 3. Electron density n(z) in the vicinity of separated grains; l is the grain boundary dilatation

Helium in the host metal interacts mainly with the electron gas; the direct interaction of helium atoms with the screened metal ions is insignificant. The energy variation associated with the introduction of helium at the boundary depends only on the local electron density. The energy shift of the electron ground state of the metal with the introduction of a helium atom is equal to [9]

$$E_{at} = \alpha n(z,l)\,, \qquad (5)$$

where α = 5,51 in atomic units (ħ = e = m =1); the unite of length is the Bohr radius a_0 equal to the most probable distance between the proton and electron in a hydrogen atom in its ground state; the unite of energy is e^2/a_0 = 27,2 eV.

As was shown by Gerasimenko et al [9] the total electron density at the center of the gap is equal to

$$n(l) = n_0 \exp\left(-q_0 l / 2\sqrt{1-\lambda}\right), \qquad (6)$$

where

$$\lambda = 1/\pi K_F \qquad (7)$$

and

$$q_0 = \sqrt{4K_F/\pi}\,. \qquad (8)$$

Here K_F is the Fermi wave vector.

It should be noted that Eq. (6) is valid for small separations. On the other hand this equation is satisfied if the variation of the electron density over a distance equal to the diameter of the helium atom is small, but this condition is possible only for a gap of finite dimensions. Fig. 4 shows the profile of the electron density at the center of grain boundary calculated using Eqs. (6) – (8).

Using the data shown in Fig. 4 and Eq. (5), we can obtain the dependence of the energy of solution of a helium atom at grain boundaries of general type (Fig. 5).

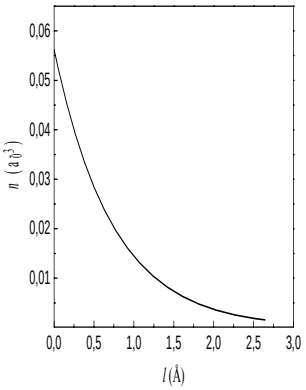

Fig. 4. Dependence of the electron density at the center of grain boundary on the grain boundary dilatation

As one can see that the energy of solution varies in the wide range of 1,809…6,334 eV. It is worth emphasizing that to the best of our knowledge, up to now, there are neither theoretical nor experimental data on the energy of solution of a helium atom at grain boundaries.

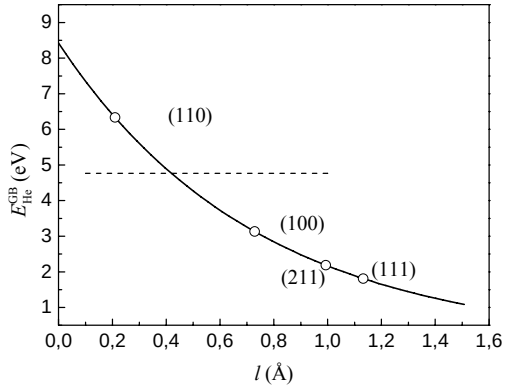

Fig. 5. Energy of solution of a helium atom at grain boundaries of general type. The dot line corresponds to the energy of solution for a helium atom at a substitutional position in an ideal crystal lattice [2]

For comparison, it can be used the theoretical data on the energy of solution for a helium atom at a substitutional position in an ideal crystal lattice. As was shown recently by Gilbert et al [2], whereas it is "conceivable that at certain boundaries, corresponding to particular orientations of neighbouring grains, the configuration adopted by He atoms may be more favourable than in the grain bulk, it is likely that our estimate for the energy of solution, evaluated using electronic-structure based methods for helium atoms occupying vacancy sites in a lattice, are fairly close to the energy of solution of helium atoms at grain boundaries". The energy of solution for a helium atom at a substitutional position in an ideal crystal lattice of tungsten is equal to 4,77 eV [2] (the dot line in Fig. 5). This value is really very close to the average of the energy of solution of helium atoms at grain boundaries shown in Fig. 5. Our studies provide insight concerning the behavior of polycrystalline radiation materials under reactor conditions at high helium levels and also will provide valuable theoretical data for continued modeling efforts of the radiation response.

CONCLUSIONS

1. The relation between the potential energy and an intergrain separation (grain-boundary dilatation) was determined by method of mathematical modeling in reciprocal space.

2. The dependence of the equilibrium GB dilatation on the GB atomic density was determined. The GB dilatation monotonically decreased with increasing of the GB atomic density.

3. Dependence of the electron density at the center of grain boundary on the grain boundary dilatation was used to obtain the dependence of the energy of solution of a helium atom at grain boundaries of general type. The average of the energy of solution of helium atoms at grain boundaries is close to the energy of solution for a helium atom at a substitutional position in an ideal crystal lattice of tungsten.

REFERENCES

1. S.L. Dudarev, J.-L. Boutard, R. Lässer, M.J. Caturla, P.M. Derlet, M. Fivel, C.-C. Fu, M.Y. Lavrentiev, L. Malerba, M. Mrovec, D. Nguyen-Manh, K. Nordlund, M. Perlado, R. Schäublin, H. Van Swygenhoven, D. Terentyev, J. Wallenius, D. Weygandm, F. Willaime. The EU programme for modelling radiation effects in fusion reactor materials: An overview of recent advances and future goals // *Journal of Nuclear Materials*. 2009, v. 386-388, p. 1-7.

2. M.R. Gilbert, S.L. Dudarev, S. Zheng, L.W. Packer, J.-Ch. Sublet. An integrated model for materials in a fusion power plant: transmutation, gas production, and helium embrittlement under neutron irradiation // *Nuclear Fusion.* 2012, v. 52, p. 083019 (12 p).

3. L. Zhang, X. Shu, S. Jin, Y. Zhang, G.-H. Lu. First-principles study of He effects in a bcc Fe grain boundary: site preference, segregation and theoretical tensile strength // *J. Phys.: Condens. Matter.* 2010, v. 22, p. 375401 (8 p).

4. A.S. Bakai, A.N. Timoshevskii, B.Z. Yanchitsky. On chemical bonding and helium distribution in hcp beryllium // *Low Temp. Phys*. 2011, v. 37, p. 791-797.

5. A.P. Sutton and R.W. Ballufi. *Interfaces in crystalline materials*. Oxford: Clarendon Press, 1995, 819 p.

6. I.M. Mikhailovskij, T.I. Mazilova, V.N. Voyevodin, A.A. Mazilov. Inherent strength of grain boundaries in tungsten // *Physical Review B.* 2011, v. 83, p. 134115 (7 p).

7. I.M. Mikhailovskij, N. Wanderka, V.A. Ksenofontov, T.I. Mazilova, E.V. Sadanov, and A.A. Mazilov. The ω structure of the lateral twin boundary in tungsten // *Philosophical Magazine Letters.* 2007, v. 87, p. 743-750.

8. T.I. Mazilova, V.A. Ksenofontov, V.N. Voyevodin, E.V. Sadanov, I.M. Mikhailovskij. Mechanical recrystallization of ultra-strength tungsten nanoneedles // *Philosophical Magazine Letters.* 2011, v. 91, p. 304-312.

9. V.I. Gerasimenko, I.M. Mikhailovskij, I.M. Neklyudov, A.A. Parkhomenko, and O.A. Velikodnaya. Changes in the structure of grain boundaries, induced by the absorption of helium, and helium embrittlement // *Technical Physics*. 1998, v. 43, p. 803-808.

Статья поступила в редакцию 04.09.2013 г.

ОПРЕДЕЛЕНИЕ ЭНЕРГИИ РАСТВОРЕНИЯ АТОМОВ ГЕЛИЯ В ГРАНИЦАХ ЗЕРЕН ОБЩЕГО ТИПА

Т.И. Мазилова, Е.В. Саданов, В.Н. Воеводин, О.В. Дудка, А.А. Мазилов, И.М. Михайловский

Методом математического моделирования в обратном пространстве определена связь потенциальной энергии границ зерен общего типа с зернограничной дилатацией в вольфраме. Показано, что электронная плотность в центре границы зависит от равновесной зернограничной дилатации и атомной плотности в плоскости границы. Определена энергия растворения атомов гелия в различных границах кручения общего типа.

ВИЗНАЧЕННЯ ЕНЕРГІЇ РОЗЧИНЕННЯ АТОМІВ ГЕЛІЮ В МЕЖАХ ЗЕРЕН ЗАГАЛЬНОГО ТИПУ

Т.І. Мазілова, Є.В. Саданов, В.М. Воєводін, О.В. Дудка, О.О. Мазілов, І.М. Михайловський

Методом математичного моделювання в зворотному просторі визначено зв'язок потенційної енергії меж зерен загального типу і зерномежевою дилатацією у вольфрамі. Показано, що електронна густина в центрі межі залежить від рівноважної зерномежевої дилатації та атомної густини в площині межі. Визначена енергія розчинення атомів гелію в різних межах кручення загального типу.