The influence of transition metal solutes on the dislocation core structure and values of the Peierls stress and barrier in tungsten

G D Samolyuk, Y N Osetsky and R E Stoller

Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
E-mail: samolyukgd@ornl.gov

Received 1 August 2012, in final form 31 October 2012
Published 29 November 2012
Online at stacks.iop.org/JPhysCM/25/025403

Abstract

Several transition metals were examined to evaluate their potential for improving the ductility of tungsten. The dislocation core structure and Peierls stress and barrier of 1/2⟨111⟩ screw dislocations in binary tungsten–transition metal alloys (W₁₋ₓTMₓ) were investigated using density functional theory calculations. The periodic quadrupole approach was applied to model the structure of the 1/2⟨111⟩ dislocation. Alloying with transition metals was modeled using the virtual crystal approximation and the applicability of this approach was assessed by calculating the equilibrium lattice parameter and elastic constants of the tungsten alloys. Reasonable agreement was obtained with experimental data and with results obtained from the conventional supercell approach. Increasing the concentration of a transition metal from the VIIIA group, i.e. the elements in columns headed by Fe, Co and Ni, leads to reduction of the C′ elastic constant and increase of the elastic anisotropy A = C₄₄/C'. Alloying W with a group VIIIA transition metal changes the structure of the dislocation core from symmetric to asymmetric, similarly to results obtained for W₁₋ₓReₓ alloys in the earlier work of Romaner et al (2010 Phys. Rev. Lett. 104 195503). In addition to a change in the core symmetry, the values of the Peierls stress and barrier are reduced. The latter effect could lead to increased ductility in a tungsten-based alloy. Our results demonstrate that alloying with any of the transition metals from the VIIIA group should have a similar effect to alloying with Re.

(Some figures may appear in colour only in the online journal)

1. Introduction

Tungsten is the prime candidate for use in the divertors of future fusion reactors because of its high melting temperature and resistance to sputtering [1, 2]. However, its lack of ductility is an impediment to its use. Low-temperature brittleness is a common problem for all metals from the VIA group, such as chromium, molybdenum and tungsten [3]. The ductility of these metals can be improved by alloying with rhenium, leading to the so-called ‘Re effect’ [4, 3, 5]. However, Re is a very rare and expensive element. It is therefore desirable to find alternative elements which provide a similar increase in ductility at lower cost. An experimental investigation of the range of candidates in the periodic table would be rather expensive, but computational materials science methods based on accurate first-principles calculations provide a very promising way to narrow the range of possible candidates. Several possible mechanisms for the Re effect have been discussed [6, 3, 7–11], and the following two mechanisms are selected as the most promising in application to monocrystals: (i) solid solution softening in which an impurity improves the mobility of the 1/2⟨111⟩ screw dislocation and (ii) enhancement of cross-slip in which an impurity modifies the dislocation core structure making it easier to cross-slip and increasing the number of possible slip planes. Both of these
are related to the effect of impurities on the dislocation core and may be amenable to investigation by density functional theory (DFT) methods even though such calculations cannot be used to directly estimate the mechanical properties. Therefore, it should be possible to define one or more calculable figures of merit that are related to a material’s elastic properties and potentially to its ductility. Among the potential figures of merit are the material’s individual elastic constants, Poisson’s ratio [12], and Peierls stress, and there is strong evidence that these parameters are also directly related to the electronic structure of the particular alloy. Since calculation of these characteristics is still too complicated for a direct first-principles approach, we use the virtual crystal approximation (discussed below) to describe the electronic structure of the tungsten alloy.

The experimentally observed strong correlation between the number of valence electrons on the solute atom and the degree of softening [13–15] points to the importance of electronic factors in solution softening [16, 17]. DFT calculations [18, 19] indicate that the ductilizing effect of Re could originate from ‘direct’ improvement of the mobility of 1/2⟨111⟩ screw dislocations [7, 20, 16, 17], either by decreasing the Peierls stress, or by enhancing the cross-slip by changing the slip plane from ⟨110⟩ to ⟨112⟩, which would increase the number of available slip planes from 6 to 12 [6, 21]. DFT calculations demonstrated that alloying with Re in a W₁₋ₓReₓ alloy leads to a transition of the 1/2⟨111⟩ screw dislocation structure from the symmetric core to asymmetric core, and to a reduction in Peierls stress [18]. Closely related results were obtained for Mo alloys with 5d transition metals [20]. The authors [20] placed solutes in a row along the 1/2⟨111⟩ dislocation core and calculated the change of stiffness associated with moving the row along the ⟨111⟩ direction. According to the results, solutes having fewer d electrons (Hf and Ta) increase the stiffness, which the authors infer to strengthen the Mo alloy, whereas those having more d electrons (Re, Os and Ir) decrease the stiffness, leading to softening.

The goal of the present investigation is to study possible substitutes for Re in alloys that will result in a similar ductilizing effect to Re. The properties of W–transition metal (TM) alloys were modeled using the virtual crystal approximation [22] (VCA). The applicability of this approach to modeling the elastic properties, structural stability and phonon properties of a W–Re alloy has been demonstrated [9, 23, 24]. The approach we use can be described as follows. First, a dislocation is placed in the effective medium representing the W–TM alloy. The properties of the dislocation in this medium are calculated exactly but for a W–TM alloy described by a virtual atom pseudopotential. The traditional approach to the VCA postulates that the effective pseudopotential of anAl₁₋ₓBₓ binary alloy is the weighted average of the elemental pseudopotentials according to V^{VCA} = (1 − x)V^{A} + xV^{B}. This approach has a set of shortcomings that are overcome in the realization proposed by Ramer and Rappe [25] used in the present work. A periodic lattice is used with the lattice parameter chosen by obtaining the zero pressure condition. This approach corresponds to a zero order contribution to the electronic system energy expansion with respect to the difference between real atomic potentials and the virtual atom. Such an approach allows separation of the so-called ‘band structure effects’, in this particular case filling of d-states, from the effect of local modification of the lattice due to W substitution. The latter is not possible in a direct supercell calculation. It has been demonstrated [18] that the dislocation properties are sensitive to modifications of this effective medium and alloying with Re leads to a sizable reduction of the Peierls stress and barrier. Within this approach, a comparison of elastic constants calculated using the VCA and supercell methods provides a verification of the VCA accuracy, as we demonstrate below.

We show that alloying with transition metals with a higher number of d electrons (VIIIA group) reduces the Peierls stress and barrier for a 1/2⟨111⟩ screw dislocation. Similarly to W–Re alloys, the dislocation core symmetry is reduced by alloying with a TM from group VIIIA. It is demonstrated that the scale of the Peierls barrier reductions is similar for all W₁₋ₓTMₓ alloys with the same ratio of electrons per atom (e/a). Although the VCA approach describes an influence of the band structure on the properties of screw dislocations, it does not describe the discrete nature of the alloy structure. However, this approach permits an assessment that can significantly reduce the range of possible solute candidates suitable for Re substitution.

This paper is organized as follows. In section 2 we briefly review the computational approaches used in the calculations. Section 3.1 describes the electronic structure of tungsten and its alloys with transition metals from the IVA, VA and VIIA groups. This is an almost complete list of possible binary solid solutions [26]. The results of modifications to the elastic constants with alloying are discussed in section 3.2. Section 3.3 presents our prediction of the core structure, Peierls barrier and Peierls stress for W₁₋ₓTMₓ alloys. Finally, the conclusions are given in section 4.

2. Computational approaches

The electronic structure within the generalized gradient approximation (GGA) of density functional theory was calculated using the QUANTUM ESPRESSO (QE) package [27]. The calculation was carried out using a plane-wave basis set and ultra-soft pseudopotentials optimized in the RRKJ scheme [28]. We used the Perdew–Wang [29] exchange–correlation functional. The Brillouin zone (BZ) summations were carried out over a 24 × 24 × 24 BZ grid for the system with one unit cell and a 16 × 16 × 16 grid for the supercell containing 2 × 2 × 2 unit cells, with electronic smearing with a width of 0.02 Ryd applied according to the Methfessel–Paxton method. The plane-wave energy cut-off of 42 Ryd allows an accuracy of 0.2 m Ryd/atom to be reached. As a realization of the VCA for the pseudopotential method, we used the scheme proposed by Ramer and Rappe [25]. This is based on the self-consistent determination of averaged all-electron properties which guarantee exact agreement of the proper averaged all-electron eigenvalues for the particular configuration of the virtual atom and yields the proper
Figure 1. The [111] projection of the dislocation dipole unit cell, where atoms are shown by circles and the arrows correspond to differential displacements.

Figure 2. DOS for pure W, blue solid line, W_{0.9375}Re_{0.0625}, red dashed line, and W_{0.9375}Zr_{0.0625}, green dash-dotted line, calculated using the VCA.

Averaged atomic size. The elastic constants were calculated from the total energies obtained for the set of unit cell deformations [30].

We used a periodic quadrupolar arrangement for a 1/2⟨111⟩ screw dislocation [31] in the cell with basis vectors \( \mathbf{b}_1 = 9\mathbf{u}_1, \mathbf{b}_2 = 5\mathbf{u}_2 \) and \( \mathbf{b}_3 = \mathbf{u}_3 \), where \( \mathbf{u}_1 = [110], \mathbf{u}_2 = [1\bar{1}2] \) and \( \mathbf{u}_3 = 1/2[1\bar{1}1] \). An appropriate choice of lattice vectors [31] reduces the quadrupole cell to half the size, and we therefore used a cell with basis vectors of \( \mathbf{h}_1 = (\mathbf{u}_1 + \mathbf{u}_2 + \mathbf{u}_3)/2, \mathbf{h}_2 = \mathbf{b}_2 \) and \( \mathbf{h}_3 = \mathbf{b}_3 \) and 135 atoms. This unit cell contains only two dislocations with opposite Burgers vectors (figure 1). It was demonstrated earlier that this cell size is large enough to reproduce such characteristics of the dislocations as the Peierls stress and barrier [32–38] reasonably well if the elastic interaction correction is included. We are interested in how the barriers change with solute concentration and therefore the above correction was not included since it is the same for all concentrations. For the dislocation calculation, the BZ summation was carried out over a 1 × 2 × 8 BZ grid [18] and the initial structure was relaxed until the forces were smaller than 0.0005 Ryd Å⁻¹.

3. Results

3.1. Electronic structure

The electronic densities of states (DOS) calculated using the VCA are presented in figure 2 (colored online) for pure tungsten (blue solid line) and two tungsten alloys, one with 6.25% Re (red dashed line) and the second one with 6.25% Zr (green dash-dotted line). The zero energy on this plot corresponds to occupation of electronic bands by six electrons. Thus, for pure tungsten, zero energy corresponds to the Fermi level. The Fermi energy is placed in the pseudo-gap between the bonding and antibonding d-states. As can be seen from figure 2, alloying with Re or Zr does not produce sizable changes in the DOS, at least in the VCA approach. The substitution of tungsten with 6.25% Re leads to an upwards shift of the Fermi energy, shown by a red vertical line. The area under the DOS between zero energy and the W_{0.9375}Re_{0.0625} Fermi energy corresponds to 0.0625 additional electrons, i.e., occupation of each virtual atom by an additional 0.0625 electrons. Correspondingly, alloying with atoms that have a lower number of electrons, such as Zr, leads to a downward shift of the Fermi energy, shown by a vertical green line, and each virtual atom is occupied by 0.0625 fewer electrons.

Such a modification of the electronic structure in tungsten alloys can be described using the rigid band approximation [22]. This approach assumes that alloying does not change the DOS but shifts the Fermi level, so the occupation of each virtual atom corresponds to the average number of electrons per atom (e/\( a \)) in the alloy. Thus, within this approximation, all alloys with the same (e/\( a \)) value have the same properties. The concentration of different alloying

---

3
where $Z_{\text{TM}}$ is the number of valence electrons of the alloying TM, $Z_W$ is the number for tungsten. Although this approach has limited accuracy, it can be very useful for qualitative estimation of the change in such properties as the elastic constants or Peierls barrier. It should be mentioned that alloying of tungsten with transition metals with a higher number of d electrons, metals from the VIIA and VIIIA groups, fills bonding d-states and reduction of cohesive energy and increase of Wigner–Seitz radius with filling of antibonding states [39].

The VCA approach could be quite inaccurate for describing the properties of disordered substitutional metallic alloys, especially for transition metals [22], and therefore the accuracy of this approach should be analyzed in each particular case. In order to verify the accuracy of the VCA we compared its results with those obtained using a supercell approach. The supercell contained $2 \times 2 \times 2$ cubic unit cells with one tungsten atom substituted by a solute atom. Thus, the solute concentration corresponded to 6.25%. In figure 3, the DOS calculated using the supercell (blue line) and VCA models (red line) are presented for W$_{1-x}$Fe. The DOS calculated using the VCA approach is very close to the supercell result. Comparisons of the elastic properties calculated using the two approaches will be discussed below.

### 3.2. Elastic constants

The modification of the elastic properties in W–Re alloys has been widely investigated both experimentally [40] and theoretically [23, 24]. Here we expand these investigations to a wide set of tungsten-based alloys. The results for the equilibrium lattice constant, $a$, bulk modulus, $B$, and elastic constants, $C_{ij}$, are presented in table 1. For the elastic constants, the largest difference between the calculated and experimental values was obtained for $C_{11}$ and is about 13% for the VCA calculations and slightly larger for the supercell calculations (SC). The agreement between the VCA and SC results for W alloys with Zr, Ta and Re is very good and the differences for elastic constants do not exceed 2%. However, this difference increases for alloys with solute atoms with a larger number of valence electrons. For example, for the Fe-family (Fe, Ru and Os) the difference is about 5%, while for the Co- (Co, Rh and Ir) and Ni-families (Ni, Pd and Pt) the difference increases to 12%–15%. Since we investigate the reduction of the Peierls stress and barrier for alloys in which the number of valence electrons per atom $(e/a)$ corresponds to 10% of Re or smaller, the elastic properties of the alloys should be described with an accuracy similar to that of Re of 5% or less. As discussed above, alloying of tungsten with transition metals with a higher number of d electrons, metals from the VIIA and VIIIA groups, fills bonding d-states. According to the general results obtained for transition metals [39, 22], this filling leads to a decrease of the lattice parameter. The calculated results for W$_{1-x}$Re$_x$ alloys reproduce this general tendency (see table 2) and agree with experiment [40].

![Figure 3. W$_{0.9375}$Fe$_{0.0625}$ DOS per atom calculated using a $2 \times 2 \times 2$ supercell model, blue dashed line, and the VCA, red solid line. The Fermi energy corresponds to zero.](image)

### Table 1. Comparison of the lattice parameter ($a$) in Å, bulk modulus ($B$) and elastic constants ($C_{ij}$) in GPa calculated using the VCA and supercell (SC) approaches for W$_{1-x}$TM$_x$.

| TM   | Approach | $a$  | B   | $C_{ij}$ | $C_{11}$ | $C_{12}$ |
|------|----------|------|-----|---------|---------|---------|
| pure W | VCA      | 3.1903 | 304 | 160 | 141 | 518 | 197 |
|       | SC       | 3.1896 | 308 | 157 | 139 | 517 | 203 |
| Zr    | VCA      | 3.2095 | 287 | 153 | 126 | 491 | 185 |
|       | SC       | 3.2079 | 286 | 150 | 127 | 489 | 186 |
| Ta    | VCA      | 3.1946 | 298 | 161 | 136 | 513 | 191 |
|       | SC       | 3.1963 | 308 | 157 | 135 | 517 | 203 |
| Fe    | VCA      | 3.1802 | 284 | 132 | 128 | 459 | 196 |
|       | SC       | 3.1716 | 300 | 140 | 132 | 487 | 207 |
| Co    | VCA      | 3.1788 | 284 | 125 | 115 | 450 | 200 |
|       | SC       | 3.1725 | 297 | 129 | 131 | 469 | 211 |
| Ni    | VCA      | 3.1830 | 279 | 116 | 126 | 434 | 202 |
|       | SC       | 3.1743 | 295 | 126 | 131 | 463 | 211 |
| Ru    | VCA      | 3.1772 | 308 | 142 | 142 | 498 | 213 |
|       | SC       | 3.1842 | 301 | 135 | 137 | 481 | 211 |
| Rh    | VCA      | 3.1710 | 309 | 135 | 141 | 490 | 219 |
|       | SC       | 3.1862 | 298 | 124 | 133 | 462 | 215 |
| Pd    | VCA      | 3.1639 | 310 | 129 | 139 | 482 | 224 |
|       | SC       | 3.1901 | 293 | 116 | 131 | 448 | 216 |
| Re    | VCA      | 3.1857 | 308 | 151 | 144 | 510 | 207 |
|       | SC       | 3.1859 | 308 | 150 | 143 | 508 | 208 |
| Os    | VCA      | 3.1809 | 312 | 143 | 146 | 503 | 216 |
|       | SC       | 3.1848 | 307 | 136 | 144 | 489 | 216 |
| Ir    | VCA      | 3.1736 | 316 | 147 | 148 | 513 | 218 |
|       | SC       | 3.1865 | 304 | 125 | 140 | 470 | 221 |
| Pt    | VCA      | 3.1687 | 317 | 132 | 148 | 494 | 229 |
|       | SC       | 3.1917 | 299 | 113 | 135 | 449 | 223 |
Table 2. Experimental and calculated (based on the VCA) values of the lattice parameter \(a\) in \(\text{Å}\), bulk modulus \(B\) in GPa for \(W_{1-x}TM_x\). The concentration for all TMs except Re is chosen to keep the number of electrons per atom \((e/a)\) equal to 6.10.

| TM   | \(x\) | \(a\) | \(B\) | \(C'\) | \(C_{44}\) | \(C_{11}\) | \(C_{12}\) |
|------|------|------|------|------|------|------|------|
| Re   | 0.0000 | 3.1903 | 304 | 160 | 141 | 518 | 197 |
| W    | 0.0000 | 3.1659 | 314 | 164 | 163 | 533 | 205 |
| Ta   | 0.0500 | 3.1880 | 306 | 156 | 142 | 514 | 202 |
| Fe   | 0.0500 | 3.1866 | 307 | 153 | 143 | 512 | 205 |
| Ru   | 1.0000 | 3.1831 | 310 | 146 | 145 | 504 | 212 |
| Os   | 0.3000 | 3.1689 | 322 | 130 | 156 | 495 | 235 |
| Rh   | 1.0000 | 3.1317 | 350 | −30 | 163 | 309 | 370 |
| Zr   | 0.0250 | 3.1972 | 297 | 161 | 136 | 511 | 190 |
| Zn   | 0.0500 | 3.1936 | 299 | 162 | 137 | 515 | 191 |
| Fe   | 0.0250 | 3.1849 | 296 | 148 | 136 | 494 | 198 |
| Ru   | 0.0250 | 3.1846 | 306 | 153 | 141 | 510 | 204 |
| Os   | 0.0250 | 3.1862 | 307 | 153 | 143 | 511 | 205 |
| Ir   | 0.0167 | 3.1849 | 308 | 154 | 143 | 512 | 205 |

According to the rigid band model discussed in section 3.1, the parameter that determines the elastic properties of \(W_{1-x}TM_x\) alloys is the number of electrons per atom, \(e/a\), calculated for \(W_{1-x}TM_x\) using the VCA.

3.3. The dislocation core structure, Peierls stress and Peierls barrier

In bcc structures \(1/2\{111\}\) screw dislocations have three nonequivalent core configurations, which are referred to as ‘easy’, ‘hard’ and ‘split’ [42, 43, 33, 44]—stable and two metastable, respectively. These configurations can be obtained for a given Burgers vector \(\vec{b}\) by placing the core origin at specific positions. Recently, it was demonstrated that in bcc Fe the lowest energy is the symmetric ‘easy’ core configuration, then the symmetric ‘hard’ core and the highest energy is the ‘split’ core configuration [45]. In contrast to Fe, for the case of W we determined that the symmetric ‘hard’ core configuration decays into the ‘split’ core. Thus, in this paper we assume that the dislocation migrates between the ‘easy’ and ‘split’ core configurations.

Following Xu and Moriarty [46] we marked these sites as 1, 4 or 5 for ‘easy’ cores and 2 or 3 for ‘split’ cores in figure 5. The calculated structure of the ‘easy’ core configuration for a \(1/2\{111\}\) dislocation is shown in figure 5 for pure W, \(W_{0.75}\text{Re}_{0.25}\) and \(W_{0.88}\text{Fe}_{0.12}\), where the concentrations of transition metals were chosen to give the same \((e/a)\) value. The circles in figure 5 represent W atoms looking in the [111] direction, and the dislocation structure is illustrated by differential displacement (DD) maps [42]. On a DD map the
displacement of atoms in the [111] direction relative to a neighbor is plotted as an arrow connecting the atom with its neighbors. The length of an arrow is normalized so that arrows connecting two atoms correspond to displacement by $b/3$. Thus, summing the arrows in the circuit around a dislocation gives the Burgers vector. For tungsten alloys with VIIIA group TMs having the same $(e/a)$ value, the core configurations looks exactly the same as for the Re and Fe alloys. In contrast, alloying with Ta or Zr produces the same core symmetry as pure tungsten. The same result was obtained for W–Ta by Li et al [19]. The core structure of pure W is symmetric, as shown in figure 5(a), i.e., the dislocation expands equally along the six $\langle 112 \rangle$ directions, similarly to results obtained earlier [18].

Alloying with Re or any other TM with a higher number of valence electrons leads to a change of the dislocation slip plane and a decrease in the value of the Peierls stress $\sigma_p$ [18]. Following a widely used technique [49], we apply pure shear strain in the $\langle 111 \rangle$ direction, which results in a stress that has $\sigma_{zx}$ as its main component; the influence of $\sigma_{yx}$ can be neglected since $\sigma_{yx}/\sigma_{zx} = 0.04$ for pure W. The corresponding strain is produced by modification of the basis vector $\vec{h}_1$ along the $\vec{u}_3$ direction, $\vec{h}_1 = 1/2\vec{u}_1 + 1/2\vec{u}_2 + (1/2 + \varepsilon)\vec{u}_3$. Figure 6 shows the dependence of the total energy (see inset) per dislocation per Burgers vector and shear stress as a function of strain, $\varepsilon$.

For small strains, i.e. in the elastic regime, the energy increases as $\varepsilon^2$. At larger $\varepsilon$ the energy dependence deviates from a square dependence and abruptly drops. This drop in energy is caused by a jump of the dislocation core to the next stable ‘easy’ core neighboring position ($1 \rightarrow 4$). The corresponding stress and strain are considered to be the
Peierls stress $\sigma_p$ and strain $\varepsilon_p$. Alloying with both Re and Fe reduces the values of $\varepsilon_p$ and $\sigma_p$. For Fe this reduction is even larger than for Re although the solute concentrations corresponds to the same $c/a$ value in both cases. The absolute value of $\sigma_p$ (equal to 1.71 GPa for pure tungsten (table 3)) is somewhat lower than those obtained earlier [18], which were 2.09 GPa using QE and 2.37 GPa using VASP. The difference is attributed to the use of different types of pseudopotentials, ultra-soft in our case and norm-conserving (QE) and PAW (VASP) in Romaner et al [18], and the higher accuracy obtained using our larger plane-wave energy cut-off of 42 Ryd compared to 30 Ryd (QE calculations) and 16.4 Ryd (VASP calculations) [18]. Moreover, the norm-conserving pseudopotential would require an even larger cut-off energy than the ultra-soft one. The relative reduction of $\sigma_p$ is 20% for Re and 36% for Fe. A larger reduction of $\sigma_p$ in tungsten–iron alloys correlates with the larger reduction of $C'$ modulus caused by alloying with Fe (figure 4 and table 2). These results demonstrate that even if the reduction of Peierls stress and $C'$ values can be qualitatively understood as arising from a filling of $d$-states in tungsten by additional electrons from group VIII solutes, some other element-specific mechanism exists. It should be mentioned that the solubility limit of Fe in W is around 2%, and if the concentration of Fe is limited to this value the reduction of the Peierls barrier is about one half of that of the alloy with 5% Fe. For the W–Ru alloy with a solubility limit of 3%, $\sigma_p$ is reduced by 6%. This result is consistent with the experimentally observed reduction of the ductile–brittle transition temperature in W–Ru alloy [50].

Table 3. A comparison of the reduction of Peierls stress calculated using the direct deformation method, $\sigma_p$ (in GPa), and from the Peierls barrier using equation (2), $\sigma_p$, in W, W$_{0.90}$Re$_{0.10}$, W$_{0.95}$Fe$_{0.05}$, W$_{0.96}$Fe$_{0.02}$ and W$_{0.97}$Ru$_{0.03}$.

| Alloy          | $\sigma_p$ (GPa) | $\sigma_p$ (GPa) |
|---------------|-----------------|-----------------|
| W             | 1.71            | 1.64            |
| W$_{0.95}$Zr$_{0.05}$ | 2.18            | 1.82            |
| W$_{0.90}$Re$_{0.10}$ | 1.37            | 1.15            |
| W$_{0.95}$Fe$_{0.05}$ | 1.09            | 1.05            |
| W$_{0.98}$Fe$_{0.02}$ | 1.65            | 1.40            |
| W$_{0.97}$Ru$_{0.03}$ | 1.60            | 1.35            |

between ‘easy’ and ‘split’ core configurations with the same 1 → 2 barrier. The energy dependence obtained is associated with the Peierls barrier and the Peierls stress is given by the maximum gradient of this function,

$$\sigma_p = \frac{1}{b} \frac{dV}{dR_c} \bigg|_{\max} ,$$

(2)

where $b$ is the Burgers vector, $V$ is the energy per unit length of a straight dislocation and $R_c$ is the distance along the dislocation core path for the move from 1 to 2. $R_c$ equals 0 for position 1 and $\sqrt{2a}/3$, where $a$ is the lattice parameter, for position 2. We use the drag method, also called the reaction coordinate method [46], to move the dislocation from the 1 (‘easy’) to the 2 (‘split’) core configuration. According to this method, the $z$-coordinates of atoms in two columns around both cores in the modeling cell, shown by the purple circles in figure 5(a), are fixed so that $z = z_0 + (1 - r_c)z_1$, where $z_0$ and $z_1$ correspond to the $z$-coordinates of the specified atoms in the ‘easy’ and ‘split’ core configurations respectively, and $r_c = R_c/\sqrt{2a}/3$ is the so-called reaction coordinate. In the initial implementation [46], the authors fix the $z$-coordinate of the atom that has the largest displacement resulting from the movement of the dislocation core. However, from our experience the atomic relaxation convergence increases if we fix the $z$-coordinates of any two of the three atoms surrounding site 2 in figure 5(a). In order to avoid any changes in the elastic interaction between dislocations, both cores are moved simultaneously. The results obtained for the Peierls barrier changes are presented in figure 7 for pure tungsten and alloys of tungsten with Re, Fe, Ru and Zr. In order to demonstrate that the ‘split’ core configuration corresponds to a metastable state, we calculated the potential barrier using a small reaction coordinate step for pure tungsten around $r_c = 1$. As can be seen from the results presented in the upper inset in figure 7, the ‘split’ core configuration corresponds to a local minimum in the potential energy. When normalized using the values for pure tungsten, the shape of the Peierls barrier for the alloys is shown to be similar to that for tungsten and quite insensitive to solute type and concentration, see the lower inset of figure 7. In all these alloys, the results yield a single barrier. For alloys with Os, Ir, Pt, Ru, Rh, Pd, Co and Ni the total energy was calculated for the ‘easy’ core (reaction coordinate, $r_c = 0$) and ‘split’ core ($r_c = 1$). Since the shape of the Peierls barrier is insensitive to the type of solute, the difference between these energies provides an estimate of the value of the Peierls barrier, as shown in figure 8.
Figure 7. The calculated Peierls barrier, where the reaction coordinate, $r_c$, is equal to 0 for the ‘easy’ core configuration and 1 for the ‘split’ core. The curves are normalized in the central inset. The detailed structure of the calculated Peierls barrier in pure W around the maximum is shown in the inset at the upper right.

The reduction of the Peierls barrier observed in these calculations correlates well with the reduction in Peierls stress estimated in the deformation simulation described above. Alloying with Re or any group VIII transition metal at a concentration that corresponds to $(e/a) = 6.10$ reduces the barrier by 25%. Fe reduces the Peierls barrier even more significantly, whereas Zr increases the barrier. This is consistent with the effect obtained for Mo alloys with 5d transition metals in which placing a row of solute atoms with a higher number of valence d electrons along the dislocation core reduces the stiffness and a row of atoms with a lower number increases the stiffness [20].

The Peierls stress calculated using the direct deformation method, $\sigma_p$, and from the Peierls barrier using equation (2), $\tilde{\sigma}_p$, are presented in table 3. For all alloys the Peierls stress values obtained from the Peierls barrier are lower than those from the direct method. The difference is largest, 14%, for W alloys with 10% Re or 2% Fe. Thus, for the $\sigma_p$ results, introduction of 2% Fe to tungsten reduces the Peierls stress by 12%, while for the pure W and W alloy with 5% of Fe it is reduced by less than 5%. Gröger and Vitek [52] connected the discrepancy in the results of the two methods with the fact that both the drag and nudged elastic band [53] (NEB) methods guarantee that images of the system are distributed uniformly along the minimum energy path and do not imply that the dislocation position is distributed along this path. In order to overcome this problem, the authors introduced a modified NEB [52] method which gives a Peierls stress that agrees within 8% with the directly calculated stress. However, we believe that the 14% accuracy obtained in our calculation is reasonably good considering that it maintains the same trend in $\sigma_p$. It should be mentioned that problems with direct application of drag or NEB methods can be more substantial. According to the modeling result obtained in the deformed cell, the dislocation core structure is slightly modified with increase of deformation and then jumps directly to next ‘easy’ core position. The dislocation core is not observed in the metastable, ‘split’ core position. Thus the agreement between the data presented in table 3 gives support to application of the drag method to calculation of the Peierls stress.

The reduction of the Peierls stress/barrier due to alloying with transition metals with a higher number of valence electrons and the increase for a lower number of valence electrons is supported by existing experimental data. Hardening was observed in W–Zr alloys [54] and softening in W–Re/Ir alloys [8]. Very interesting experimental results for Mo alloys with group VIII A 3d transition metals were presented by Hiraoka et al [13]. The authors reported a decrease of yield strength with addition of any element from group VII A, Fe, Co, Ni or 4d Pd. The authors concluded that this effect could be well understood in terms of the number of valence electrons of the alloying elements, and that the effect of atomic size mismatch was secondary and minor. Although the value of the yield strength is not directly related to the ductility, the observed correlation of properties with the e/a value supports the validity of our calculation using the VCA approach.

4. Conclusions

The influence of alloying tungsten with transition metal solutes on the elastic properties and the properties of the $1/2\langle111\rangle$ screw dislocation was investigated based...
on electronic structure calculations. In comparison with a standard supercell method, we demonstrated that the virtual crystal approximation gives a fairly good description of such alloying, especially in the case of 4d and 5d transition metals. For the case of alloying with transition metals from group VIIIA, the modification of elastic constants, Peierls stress and barrier can be understood within the rigid band approximation. This means that alloys with TM concentrations leading to the same number of electrons per atom exhibit a similar reduction of the C' modulus and elastic anisotropy A. Together with this modification of the elastic moduli the values of the Peierls stress and barrier are reduced by alloying with transition metals from group VIIIA. In addition to the Peierls barrier reduction, alloying with any metal from this group changes the 'easy' core dislocation structure from the symmetric to the asymmetric configuration. This similarity allows us to conclude that the search for an alternative to Re could be reduced to transition metals from the group VIIIA.

Acknowledgments

This work was supported by the US Department of Energy Office of Fusion Energy Sciences. This research used resources of the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the US Department of Energy.

References

[1] El-Guebaly L, Kurtz R, Rieth M, Kurishita H, Robinson A and Team A 2011 Fusion Sci. Technol. 60 185
[2] Nygren R, Raffray R, Whyte D, Urickson M, Baldwin M and Snead L 2011 J. Nucl. Mater. 417 451
[3] Klopp W D 1969 J. Met. 21 23
[4] Geach J C and Hughes J E 1956 Plansee Proc. (Oxford: Pergamon).
[5] Savitskii E M, Tylkina M A and Povarova K V 1965 Rheinian-Based Alloys (Moscow: Nauka)
[6] Edington J W, Gilbert A and Klein M J 1966 NASA CR-81225
[7] Raffo P 1969 J. Less-Common Met. 17 133
[8] Luo A, Jacobsson D and Shin K 1991 Int. J. Refrac. Met. Hard Mater. 10 107
[9] Gornostyrev Y N, Katsnelson M I, Peschanskikh G V and Trefilov A V 1991 Phys. Status Solidi B 164 185
[10] Trefilov V I, Milman Y V and Firsov S V 1975 Physics of Refractory Metal Strength (Kiev: Naukova Dumka)
[11] Kudryumova G G, Milman Y V and Trefilov V I 1980 Electronic Structure and Physico-Chemical Properties of Refractory Compounds and Alloys (Kiev: Naukova Dumka)
[12] Gao M C, Dogan ¨O N, King P, Rollett A D and Widom M 2008 JOM 60 61
[13] Hiraoka Y, Ogusu T and Yoshizawa N 2004 J. Alloys Compd. 381 192
[14] Klopp W D 1975 J. Less-Common Met. 42 261
[15] Stephens J R and Witzke W R 1975 J. Less-Common Met. 41 265
[16] Medvedeva N I, Gornostyrev Y N and Freeman A J 2005 Phys. Rev. Lett. 94 136402
[17] Medvedeva N I, Gornostyrev Y N and Freeman A J 2007 Phys. Rev. B 76 212304
[18] Romaner L, Ambrosch-Draxl C and Pippan R 2010 Phys. Rev. Lett. 104 195503
[19] Li H, Wurster S, Motz C, Romaner L, Ambrosch-Draxl C and Pippan R 2012 Acta Mater. 60 748
[20] Trinkle D R and Woodward C 2005 Science 310 1665
[21] Garfinke M 1966 NASA TN D-3190 1
[22] Faulkner J S 1982 Prog. Mater. Sci. 27 1
[23] Persson K, Ekman M and Grimvall G 1999 Phys. Rev. B 60 9999
[24] Ekman M, Persson K and Grimvall G 2000 J. Nucl. Mater. 278 273
[25] Ramer N J and Rappé A M 2000 Phys. Rev. B 62 R743
[26] Lassner E and Schubert W-D 1999 Tunneling—Properties, Chemistry, Technology of the Element, Alloys, and Chemical Compounds (Berlin: Springer)
[27] Giannozzi P et al 2009 J. Phys.: Condens. Matter 21 395502
[28] Rappé A M, Rabe K M, Kaxiras E and Joannopoulos J D 1990 Phys. Rev. B 41 1227
[29] Perdew J P and Wang Y 1992 Phys. Rev. B 45 13244
[30] Mehli M J, Osburn J E, Papaconstantopoulos D A and Klein B M 1990 Phys. Rev. B 41 10311
[31] Bigger J R K, McInnes D A, Sutton A P, Payne M C, Stich I, King-Smith R D, Bird D M and Clarke L J 1992 J. Phys. Lett. 69 2224
[32] Segall D, Arias T, Strachan A and Goddard W 2001 J. Comput.-Aided Mater. Des. 8 161
[33] Ismail-Beigi S and Arias T A 2000 Phys. Rev. Lett. 84 1499
[34] Segall D E, Strachan A, Goddard W A, Ismail-Beigi S and Arias T A 2003 Phys. Rev. B 68 014104
[35] Frederiksen S L and Jacobsen K W 2003 Phil. Mag. A 83 365
[36] Li J, Wang C-Z, Chang J-P, Cai W, Bulatov V V, Ho K-M and Yip S 2004 Phys. Rev. B 70 104113
[37] Ventelon L and Willaime F 2007 J. Comput.-Aided Mater. Des. 14 85
[38] Odbadarkh K, Rusanu A, Stocks G M, Samolyuk G D, Eisenbach M, Wang Y and Nicholson D M 2011 J. Appl. Phys. 109 07E159
[39] Moruzzi V L, Williams A R and Janak J F 1977 Phys. Rev. B 15 2854
[40] Ayres R A, Shannette G W and Stein D F 1975 J. Comput. Phys. 15 1526
[41] Massalski T B, Murray J L, Bennett L H and Baker H 1986 Binary Alloy Phase Diagrams (Metals Park, Ohio: American Society for Metals)
[42] Vitek V 1974 Cryst. Letters Discects 5 1
[43] Xu W and Mortari J A 1996 Phys. Rev. B 54 6941
[44] Takeuchi S 1979 Phil. Mag. A 39 661
[45] Itakura M, Kaburaki H and Yamaguchi M 2012 Acta Mater. 60 3698
[46] Xu W and Mortari J A 1998 Comput. Mater. Sci. 9 348
[47] Hirth J and Lothe J 1982 Theory of Dislocations (New York: Wiley-Interscience)
[48] Gröger R 2007 PhD Thesis University of Pennsylvania arXiv:cond-mat/0707.3577v1
[49] Segall D E, Arias T, Strachan A and Goddard W III 2001 J. Comput.-Aided Mater. Des. 8 161
[50] O’Dell S, McKechnie T, Shchetkovskiy A and Smirnov A 2012 Workshop on Challenges to Developing W-Based Materials for Fusion Application (UC Santa Barbara, Santa Barbara)
[51] Nabarro F R N 1947 Proc. Phys. Soc. 59 256
[52] Gröger R and Vitek V 2012 arXiv:cond-mat/111.5709v1
[53] Jonsson H, Mills G and Jacobsen K W 1998 Classical and Quantum Dynamics in Condensed Phase Simulations ed E B J Berne, G Ciccotti and D F Coker (Singapore: World Scientific) p 385
[54] Pod’yachev V N and Gavrilyuk M I 1975 Met. Sci. Heat Treat. 17 299