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***Ab initio* search for cohesion-enhancing impurity elements at grain boundaries in molybdenum and tungsten**

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Abstract

We report high throughput density functional theory (DFT) calculations to simulate segregation of *s*- and *p*-elements in Mo and W. First, the preference of solutes for interstitial or substitutional positions in the bulk is evaluated and then the segregation energies for the solutes to interstitial and different substitutional sites at a grain boundary (GB) and a free surface (FS) are computed. We show that several solutes change their site preference from substitutional to interstitial position upon segregation to the GB. With the segregation energies to GB and FS, the changes in cohesion can be calculated and GB cohesion enhancing solutes can be identified. The results show striking similarity for both W and Mo. In addition, we collected the available literature data from experimental and theoretical side, which we consequently compare to our results. From our results and the comparison to literature, we identify B, C and Be as potential alloying additions for an increased GB cohesion in Mo and W.

Keywords: tungsten, molybdenum, DFT, GB cohesion, segregation, *s*- and *p*-elements

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

1. Introduction

Many material properties are strongly affected by segregation of impurities to grain boundaries (GB). In this regard, one of the most important properties is the GB cohesion, which in

some materials decreases drastically already at very low impurity concentrations. Well known examples for such effects are e.g. hydrogen in nickel-based alloys, phosphorus in iron or sulfur in nickel. In these examples, already very low concentrations (in ppm range) can be disastrous [1, 2]. But also the opposite effect that an impurity strengthens the GB has been observed, e.g. carbon and boron in many transition metals [3, 4].

W and Mo are both refractory metals known for their high melting points, low thermal expansion coefficients, good thermal and electrical conductivity, high strength at elevated temperatures and high Young's modulus, but suffer from brittleness around room temperature owing to relatively low GB cohesion compared to bulk cohesion. This GB brittleness is intrinsic to pristine W and Mo [5, 6], yet it can be intensified by impurity segregation. Due to the specific production of W and Mo, harmful impurities cannot be completely removed and other strategies are necessary to eliminate the impurity driven GB embrittlement. Two strategies are possible: Gettering of the impurities in the bulk or replacement of harmful impurities with GB cohesion enhancing impurities. In this work we will focus on the second strategy by scanning the *s*- and *p*-elements for candidates that have a tendency for GB segregation and enhance GB cohesion at the same time.

Experimental studies on segregation in W and Mo have been performed by various authors, where most works are focused on the elements C and O. For Mo, a study by Drachinskiy *et al* [7] showed that the segregation tendency to the GB is higher for O than for C. This is in accordance with Kumar and Eyre [3], for they stated that beneficial C removes the embrittling element O from the GB, but only for much higher C concentrations than O concentrations. Kadokura *et al* [8] observed a strong increase in GB cohesion when alloying with C and also Morito [9] found that C, as well as B, increases GB cohesion. Si in Mo was investigated by Sturm *et al* [10] concluding that Si lowers the GB cohesion and leads to preferred intergranular fracture. For W, Joshi *et al* [11] found that P decreases the GB cohesion, while C and O do not influence it. This is in contrast to Smiti *et al* [12], who observed that the GB cohesion is decreased by O and increased by C. Also Benesovsky *et al* [13] reported C to be beneficial for GB cohesion. A study by Povarova *et al* [14] describes the effect of B on GB cohesion and found beneficial effects over a wide concentration range. In summary, the main findings from experiments are that O embrittles the GB, while C enhances GB cohesion and at the same time reduces the O concentration at the GB.

Also past *ab initio* studies had a special focus on C and O segregation. Two studies on impurity segregation in Mo are already available: Janisch *et al* [15] showed that B and C enhance cohesion while N and O decrease cohesion at a GB, which is in accordance with Lenchuk *et al* [16], who also predicted embrittlement for O and Si. More studies are available concerning impurity segregation in W: Zhou *et al* [17] predicted increased GB cohesion for C at GBs. Three studies by Setyawan *et al* [18–20] showed that Be, B, C, N and P should enhance GB cohesion, while O, Mg, Si and S have mixed effects on GBs. However, a study by Pan *et al* [21] promotes only B and C as GB enhancing elements, while N, O, Si, P and S are expected to decrease GB cohesion. These findings from *ab initio* theory compare well with experimental findings regarding the elements C and O: C is a cohesion enhancer, while O embrittles the GB. But overall, the picture from literature is far from being consistent with contradicting results for some elements. Further, none of these studies have investigated the preference of elements for interstitial or substitutional positions in the bulk or at the GB, which is, however, a factor strongly affecting segregation energies and strength of embrittlement (*SE*).

In this study, we present and compare the effect of solute segregation for *s*- and *p*-elements on both Mo and W. The segregation calculations are performed for one representative GB and both substitutional as well as interstitial sites are considered. We show that some solutes

retain their site preference while others change their site preference from a substitutional position in the bulk to an interstitial position at the interface. The computed SE reveals those elements that enhance cohesion in both Mo and W. As a consequence of this consistent set of data, trends for segregation of solutes are obtained and strong similarities between Mo and W are illustrated. The present data is then also compared to data from previous studies and discrepancies are discussed. With this thorough study, a set of solutes are suggested for material design in order to reduce embrittling effects and to improve GB cohesion in Mo and W.

2. Methodology

2.1. Theoretical basis

We first consider the preference of a solute for an interstitial or a substitutional position in the host bulk structure. This preference is computed by the difference in formation energy of the two respective positions:

$$\Delta E = E_{\text{sub}} - (E_{\text{int}} - E_{\text{host}}). \quad (2.1)$$

Here, E_{sub} is the total energy of a bulk slab of N atoms, where the solute atom replaces the host at a substitutional position, whereas E_{int} denotes the total energy of a bulk slab of $N + 1$ atoms, where the solute is in an interstitial position. Due to the different number of host atoms in the two slabs (N versus $N - 1$), the energy of a single host atom in its bulk structure, $E_{\text{host}} = E_{\text{pure}}/N$ has to be subtracted. The quantity E_{pure} is computed from a bulk slab of N host atoms. Our definition of ΔE is such that for negative values, the solute prefers the substitutional position, and otherwise the interstitial position. With equation (2.1), the preference for interstitial or substitutional position is evaluated for materials in thermal equilibrium. Non-equilibrium cases, such as e.g. irradiated materials, are beyond the scope of this work.

The segregation energy of a site i , E_{seg}^i , is calculated as [22]:

$$E_{\text{seg}}^i = (E_{\text{GB}}^i - E_{\text{GB}}) - (E_{\text{Bulk}}^j - E_{\text{Bulk}}), \quad (2.2)$$

where E_{GB}^i (E_{Bulk}^j) is the total energy of a GB (bulk) cell with the solute at site i (j) and E_{GB} (E_{Bulk}) is the total energy of the pure GB (bulk) cell. If a solute exhibits a positive ΔE , the bulk reference energy E_{Bulk}^j is computed for a solute in an interstitial site, while for the other solutes the reference energy is for a substitutional position. For the GB investigated, the segregation energy was calculated for three substitutional sites and one interstitial site at the GB and at the free surface (FS) which are highlighted in figure 1. In case a solute prefers a substitutional position in bulk, but its covalent radius is rather small (see figure 2), also the interstitial position at FS and GB has been tested. To keep the number of atoms in the GB with solute (E_{GB}^i) the same in such a case, one atom from the surface (atom at site 4 in panel (a) of figure 1) has been removed when a substitutional solute was placed at an interstitial position on the GB or on the FS.

The segregation of a solute to an interface lowers the interface energy by the segregation energy. This change in interface energies causes a change in GB cohesion, which is assessed through the SE of a solute. The quantity SE is computed as the difference between the segregation energy to the GB and the FS [23–25]:

$$SE = E_{\text{seg}}^{\text{GB,min}} - E_{\text{seg}}^{\text{FS,min}}. \quad (2.3)$$

Here, $E_{\text{seg}}^{\text{GB,min}}$ and $E_{\text{seg}}^{\text{FS,min}}$ denote the minimal GB segregation energy and the minimal FS segregation energy. By using the minimal segregation energies to the interfaces, we consider only the most stable states. Note that a negative SE signalizes an increase in cohesion, while a positive value signalizes a weakening of the cohesion.

2.2. Computational details

The computations were performed with the Vienna *ab initio* simulation package (VASP) [26–33] using projector augmented wave functions (PAW) and the Perdew–Burke–Ernzerhof exchange–correlation (xc) functional improved for solids (PBEsol) [34]. For an accurate treatment of the transition metals, we treated Mo and W with d electrons in the valence and s and p semi-core electrons. All solutes were modelled with s - and p -electrons in the valence, except for Na and Mg, where the p -electrons of the inner shell were included as semi-core electrons. All total energies necessary for the computation of the site preference from equation (2.1), or the segregation energy from equation (2.2) for one solute have been performed with the default energy cut-off supplied with the PAW potentials for the hardest element involved. The convergence criterion for ionic relaxation was $0.01 \text{ eV } \text{\AA}^{-1}$. We constructed the supercell for the GB along the $[110]$ and the $[101]$ direction in the GB plane, which consisted of two (-111) surfaces put together. In order to study surface segregation a $6 \text{ \AA}$ vacuum layer was added on top of the supercell. With that the dimensions of the supercell were $\sqrt{2} a_0 \times \sqrt{2} a_0 \times 23.4 a_0$, where a_0 is the lattice constant (for W $a_0 = 3.1558 \text{ \AA}$ and for Mo $a_0 = 3.1292 \text{ \AA}$ [5]). For this supercell we chose a Γ -centered $12 \times 12 \times 1$ k -point mesh. The cubic bulk reference cell containing 249 atoms plus one solute atom for substitutional and 250 atoms plus one solute for interstitial solutes, was modelled with a Γ -centered $3 \times 3 \times 3$ k -point mesh. All these settings represent parameters carefully converged with respect to the segregation energies to within 0.02 eV .

From two of our previous studies [5, 22], the $\Sigma 3[110](-111)$ GB (panel (a) in figure 1) emerged as a good model GB: The first study investigated the segregation of Re in W to many different GBs, which showed that segregation energies for this $\Sigma 3$ GB are representative for high energy GBs, despite the low Σ value of the GB. Amongst other GB properties, the second study compared GB energies in both W and Mo and proved that the $\Sigma 3[110](-111)$ GB exhibits a GB energy in the range of other high energy GBs. Because of these reasons, the $\Sigma 3[110](-111)$ GB is assumed to be a good model GB. Panel (a) of figure 1 shows the considered substitutional sites (1–3) and interstitial site (0) for FS and GB in the GB structure.

For the solutes Be, Cl and F, the relaxation lead to a special modification of the GB structure when placing the solute at site 2 or site 3. This modified GB structure is shown in panel (b) of figure 1. In particular, this transition happened in both Mo and W for Be and F when placed at site 2 and for Cl and F when placed at site 3. The modified GB structure resembles to some extent the structure with the interstitial site. The reason for the modification is most certainly the high coverage of 1 monolayer, but we assume that the general trend for segregation is not affected by this.

3. Results

3.1. Interstitial versus substitutional position in bulk

The presentation of the results is done in parallel for Mo and W, because the data for both are qualitatively very similar with some minor quantitative differences. To determine the

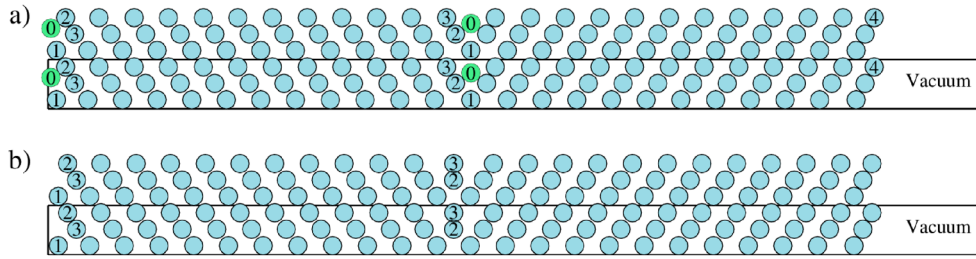


Figure 1. Panel (a) shows the GB used for the segregation calculations with numbered GB and FS sites (0 denotes interstitial sites and 1–4 substitutional sites), while panel (b) contains the geometric variant observed for some segregating elements (see text).

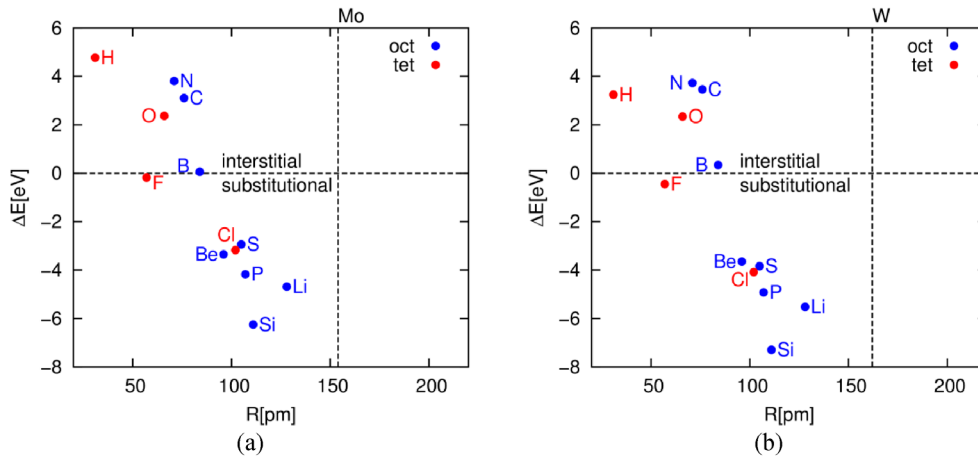


Figure 2. Difference in formation energy ΔE of solutes in bulk plotted against the covalent radius R for (a) Mo and (b) W. Solutes in blue prefer octahedral sites while solutes depicted in red prefer tetrahedral sites. If ΔE for a solute is smaller than zero, substitutional position in bulk is preferred.

preference of a solute for an interstitial or a substitutional position in the bulk, ΔE from equation (2.1) has been evaluated in Mo and W for the solutes investigated. The results are presented in figure 2, where we plot ΔE as a function of the covalent radius of the solute atom. For both Mo and W, the figure reveals an overall linear trend for an interstitial site preference of smaller solutes. Namely, H, C, N, O and B prefer interstitial positions, where the preference for the interstitial site is small for B. The other solutes prefer a substitutional position. Analyzing the type of interstitial position in more detail, we find that for H and O the tetrahedral interstitial position is energetically lower, while the other interstitial solutes favor the orthogonal interstitial position. This preference for octahedral and tetrahedral positions is in accordance with previous studies in different materials, e.g. [18, 20, 35].

For all solutes with a negative ΔE , the segregation energies are calculated with respect to a substitutional bulk position in the following. Note that the segregation energy with respect to the interstitial bulk position can be obtained by adding ΔE to the substitutional segregation energy.

3.2. Segregation to grain boundary and free surface

The results for segregation energies and SE for different sites in Mo and W are given in figures 3 and 4, respectively. We first discuss the segregation energies to the FS, which are given in panels (a) of figures 3 and 4, respectively. The strongest tendency to segregate to the FS is found for Cl with -5.9 eV/atom in Mo and -6.7 eV/atom in W, while the weakest tendencies to segregate to the FS is observed for Be and Al with segregation energies of only -0.9 and -1.3 eV/atom in Mo and W, respectively. When comparing the segregation energies in Mo with those in W, we see that the magnitude of segregation is overall higher in W. Some solutes prefer a substitutional position in bulk, but are still comparably small with respect to the host (see figure 2). For such solutes also the interstitial position at the FS has been tested as a segregation site. In some cases (F, S, Cl), this led to a stronger segregation to the FS, while for the other solutes, the relaxation led to a structure and a segregation energy similar to the relaxation when started from site 1. In general, site 1 exhibited the strongest segregation tendency for all solutes, except for F, S and Cl, where the interstitial site was preferred.

Next we concentrate on the GB segregation energies, which are plotted in panels (b) in figures 3 and 4 for Mo and W, respectively. Compared to the FS segregation energies, smaller magnitudes are observed: While Al still has the smallest tendency to segregate to the GB with values of about -0.3 eV/atom, the strongest tendency to segregate is now observed for B with about -3 eV/atom. The two well studied elements C and O also show strong tendencies to segregate to the GB, but not as strong as B. The fact that O exhibits a stronger segregation tendency than C is in accordance with experimental findings [7]. We further observe that the site preference for the substitutional position has changed. In the case of GB segregation, the preferred segregation site is site 2, except for Al in Mo and Na, Mg in W and Mo, where still site 1 is favored as for the FS segregation. In analogy to the FS, also for the GB the interstitial site was tested with the result that the same solutes (F, P, S, Cl) favor the interstitial site, including Si in W, which also shows a small preference for the interstitial site. This change in site preference for some solutes is noteworthy, for this change is currently also discussed for P in steels [36] in connection with entropy effects. Our results give the hint that a strong contribution to the site change is of purely structural origin.

Finally, we evaluate the SE , which has been obtained with equation (2.3) and is shown in panels (c) of figures 3 and 4 for Mo and W, respectively. The minimum value of SE is found for C (about -0.95 eV/atom for both W and Mo), which corresponds to a strong increase in GB cohesion. The highest SE is computed for Cl in both W and Mo. The only solutes with a negative SE are Be, B, C and N in Mo and Be, B and C in W. In case of Be, it has to be mentioned that the site with strongest strengthening is not found for site 1, but rather for site 2, which highlights the importance of including multiple sites at the GB.

4. Discussion

4.1. Analysis of observed trends

Especially for the third row elements Na to Cl, but to a lesser degree also for the second row elements from B to F, a progression of the segregation energies for the individual sites with the filling of the sp -band can be observed. The shape of this progression is different for the FS compared to the GB. Interestingly, SE , which is the difference between GB and FS segregation energies, reveals a much smoother parabolic shape. The nature of these trends is not clear at first, but in our previous work on segregation of transition elements in W and Mo [37], similar

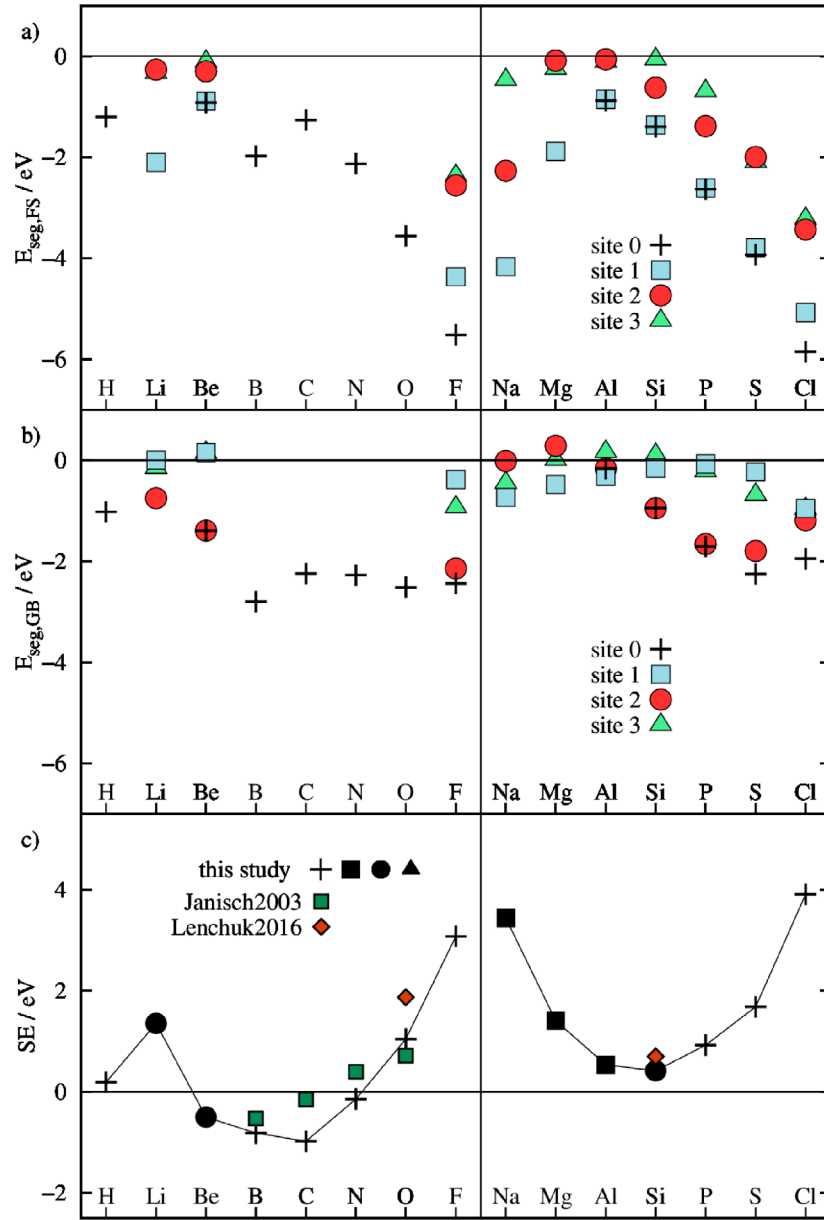


Figure 3. FS segregation energies $E_{\text{seg,FS}}^i$ (panel (a)) and GB segregation energies $E_{\text{seg,GB}}^i$ (panel (b)) for substitutional (sites 1–3) and interstitial (site 0) positions and the resulting strength of embrittlement SE for Mo (panel (c)). For the strength of embrittlement a comparison to Janisch [15] and Lenchuk [16] is given.

shapes were found upon d -band filling in agreement with several previous investigations on d -transition metals [38–40]. Our investigation strongly suggests that analogous mechanisms are at work also for sp -band filling. The mechanisms are of chemical and elastic nature and models are available in the literature to estimate their contributions. In our previous study, we relied on the Friedel model for the chemical contribution and the Eshelby model for the elastic

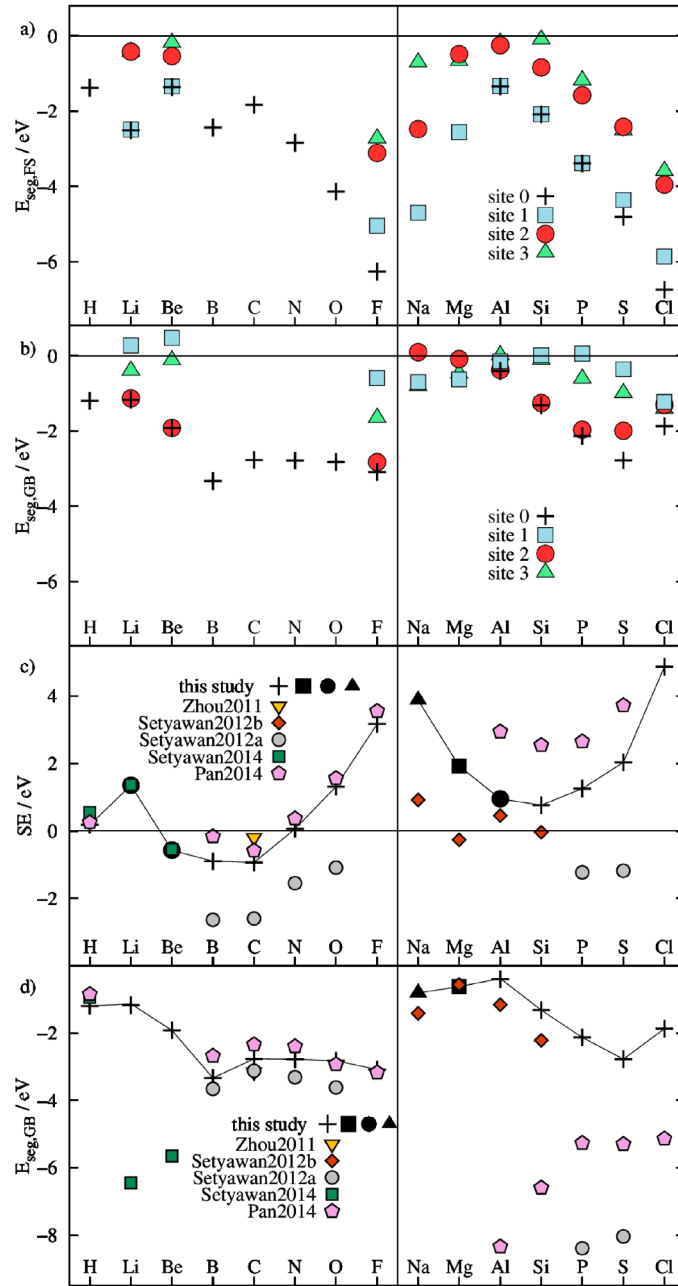


Figure 4. FS segregation energies $E_{\text{seg,FS}}^i$ (panel (a)) and GB segregation energies $E_{\text{seg,GB}}^i$ (panel (b)) for substitutional (sites 1–3) and interstitial (site 0) positions and the resulting strength of embrittlement SE for W (panel (c)). For the strength of embrittlement and the strongest GB segregation energies a comparison to values from literature (Zhou [17], Setyawan [18], Setyawan [19], Setyawan [20] and Pan [21]) is given in the panels (c) and (d)).

contribution. By combining these two models, we could partially explain the observed trends, in particular the parabolic trend for *SE*. However, some features of the DFT results, especially those for the segregation energies, could not be captured since they are beyond such simple model approaches. Since the Friedel model has been developed for *d*-elements and not for *sp*-elements, we refrain from such an analysis here and only point out the similarities between *d*- and *sp*-band filling.

A model explicitly for *sp*-interstitial solutes is Cottrell's unified theory [41], which is discussed in detail by Janisch *et al* [15] for B, C, N and O in Mo. Cottrell showed that interstitial solutes with valence states close to the Fermi energy (B, C, N) increase GB cohesion by covalent bonding, while solutes with valence states below the *d*-band (H and O) decrease GB cohesion. Janisch *et al* confirmed Cottrell's findings for B, C, N and O by analysis of the density-of-states from DFT. The parabolic shape of the *SE* with *sp*-band filling does not emerge in the work of Janisch *et al* because of the reduced set of solutes considered. Also, it has not been discussed by Cottrell *et al*.

4.2. Comparison to data from literature

We compare our results for the *SE* to the two available studies on impurity segregation in Mo for a subset of solutes, which have been investigated in those works (see panel (c)) of figure 3). In general, a good accordance is obtained. In detail, Janisch *et al* [15] predict the highest strengthening for B and a slight embrittlement for N, while our data suggest C to be the best GB cohesion enhancer and N to slightly increase GB cohesion. Nevertheless, the trend for B, C, N and O is comparable.

The data from Lenchuk *et al* [16] compares well for Si and deviates somewhat for O, for which an even stronger tendency for decohesion is predicted. These small deviations may arise from the use of a different GB ($\Sigma 5(100)[01\bar{3}]$), since especially the segregation energy to the $[01\bar{3}]$ surface is expected to differ from our segregation energy to the $[11\bar{1}]$ surface.

For W, five different papers are compared to our values for *SE* and GB segregation energies in the panels (c) and (d) of figure 4. While some features of the literature data agree quite well with our results, other parts show large differences to our results. Possible reasons for these disagreements are discussed in the following.

Zhou *et al* [17] have computed the GB segregation and *SE* for C in W at a $\Sigma 5(100)[01\bar{3}]$ GB. The GB segregation energy is comparable to our result, but the effect on cohesion shows a larger difference. Similar as for Mo, this deviation is attributed to the different FS.

Pan *et al* [21] have used the same GB as in our study, however, the study was performed with a lower solute coverage (Pan *et al*: 0.25 monolayer; this study: 1 monolayer). Nevertheless, for H and the second row solutes, both, the *SE* as well as the GB segregation energies agree well with our data except some small deviation observable for B. This indicates that the effect of coverage is negligible. Contrary to that, the data on third row solutes differs significantly. These differences may stem from the fact that Pan *et al* have treated all solutes as interstitial solutes in the bulk. However, from figure 2 we see that this is only reasonable for H, B, C, N and O (for F the difference is also small), but not for the other solutes.

When comparing to the data from Setyawan *et al* one can recognize substantial deviations for some data points. In the following we discuss the possible origins of the discrepancies. First, for the older studies [18, 19], the selected GB is a geometric variant of the $\Sigma 27(110)[5 - 52]$ GB, which, however, corresponds not to the equilibrium structure but an excited structure leading to a decrease of the inherent GB cohesion [5]. Secondly, in these old studies, changes in GB cohesion are evaluated by separating the GB always at the same GB plane, but for some

solute another fracture plane is preferred. Especially because of the second effect the SE is considerably underestimated in [18, 19] (see circles and diamonds in panel (c) of figure 4). On the other hand, the segregation energy should not be largely affected by this effect and, indeed, the data by Setyawan *et al* compares well to our results. An exception is given for Li, Be, S and P. The reason for this deviation is most probably that Setyawan *et al* have treated these solutes as interstitial solutes in the bulk, while we have shown that those elements prefer substitutional sites, which in turn led to a stronger GB segregation. Note that due to a different evaluation of the SE ⁴ the data on Li and Be for SE agrees again very well with our data.

4.3. Recommendation for material design

We are now able to identify solutes that increase GB cohesion from figures 3 and 4. In W and Mo, we expect Be, B and C to enhance GB cohesion. From the figures we see that Be will segregate to substitutional sites, while B and C will occupy interstitial position. This site preference is important when considering site competition at the GB, for example, Be will compete with other substitutional solutes, while B and C will compete with interstitial solutes. All three solutes, especially B, exhibit strong tendencies to segregate to the GB and therefore should be able to replace all embrittling solutes at the GB. Finally, we have to note that when designing a new alloy, also other effects will come into play, e.g. solute solution hardening and co-segregation of solutes that might change the segregation energies and SE of a solute.

5. Conclusion

In this work, we investigated grain boundary segregation and cohesion enhancement/reduction of all solutes from the first to the third row of the periodic table in Mo and W by means of high throughput DFT calculations. These calculations showed that the site preference for interstitial or substitutional site, as well as the trends for segregation energies and the SE are very similar for W and Mo. We identified several solute elements (P, S, F and Cl), which change from a substitutional site in the bulk to an interstitial site at the GB. The solutes Be, B and C were revealed as cohesion enhancers in both W and Mo. N shows a rather weak influence on GB cohesion while all other investigated solutes decreased GB cohesion. Similar as in our previous study on segregation of transition elements, clear trends with sp -band filling were observed, and the lowest tendency for embrittlement was always found in the center of the band. Our data agrees well with some data from literature, while other data shows substantial discrepancies. These discrepancies are rooted in a different choice of substitutional/interstitial position of the solute in the bulk and a different evaluation of the SE . The comparison with literature suggests that especially the choice for substitutional or interstitial position of the solute in the bulk is crucial, whereas the solute coverage does not strongly influence the results. From our results, Be, B and C emerge as beneficial solute elements in W and Mo, since they have the potential to displace detrimental solutes such as O, S, P or H from the GB and reduce the propensity for intergranular failure in W and Mo alloys.

⁴The strength of embrittlement is not evaluated using GB segregation energies and FS segregation energies but by computing the change in fracture energy directly.

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