Segregation of solute atoms (Y, Nb, Ta, Mo and W) in ZrB₂ grain boundaries and their effects on grain boundary strengths: a first-principles investigation

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Abstract: ZrB₂ based ultra-high temperature ceramics (UHTCs) exhibit a unique combination of excellent properties that makes them promising candidates for applications in extreme environments. Evaluating the correlation between microscopic defects and macroscopic performance of these materials is crucial for the design of UHTCs. The present work deals with a first-principles investigation on segregations of solute atoms (Y, Nb, Ta, Mo and W) in ZrB₂ grain boundaries and their influences on grain boundary strengths. Opposite segregation tendency between Y and Nb, Ta, Mo or W is obtained, where Y prefers sites with long M-B bonds, while Nb, Ta, Mo or W prefers sites with short M-B bonds. The short equilibrium M-B (M = Nb, Ta, Mo or W) bonds induce local contractions around grain boundaries, which in turn strengthens grain boundaries remarkably, thereby enhances the mechanical properties of ZrB₂ at evaluated temperatures. In contrast, segregation of Y poisons

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grain boundaries due to local expansions induced by long Y-B bonds, which will deteriorate the performance of ZrB₂ based UHTCs. The results provide useful guidelines for the design of ZrB₂ based UHTCs, since grain boundaries play a key role in determining high temperature mechanical properties.

Keywords: ZrB₂ based UHTCs; grain boundary segregation; strength; first-principles

1. Introduction

Recent interests in ZrB₂ based ultra-high temperature ceramics (UHTCs) are motivated by the development of hypersonic vehicles, in which the leading-edge and nose-tip should withstand extreme high temperature (>2000 °C) for a long service time [1-3]. Though ZrB₂ exhibits a unique combination of excellent properties, including high melting point, chemical inertness, effective wear and environmental resistance, its application in hypersonic technology is still impeded by poor resistance to thermal shock and oxidation [3] and rapid drop of flexural strength at high temperatures [4].

In ceramics, high temperature fracture frequently involves the nucleation, growth and coalescence of grain boundary located micro-cracks or cavities [5]. Similar mechanism also controls the failure of ZrB₂ based UHTCs, since the high temperature fracture is dominated by intergranular fracture [6-8]. For example, as reported by Kalish *et. al.*[6] and Bird *et. al.*[7] almost 90% or more grains craze by intergranular fracture at 1400 °C. Therefore, strengthening grain boundaries and suppressing grain

boundary sliding are crucial in improving the high temperature performance of ZrB_2 based UHTCs. Previous experiments have demonstrated that ZrB_2 based UHTCs with additives of TaSi_2 , MoSi_2 , WSi_2 or WC generally display promising retention of strength at high temperatures [4, 9-12], where evident dissolution of Ta, Mo or W into ZrB_2 grains has been reported [9-11]. The mechanism for the outstanding high temperature performance is still not well understood. Though segregation of solute atoms in grain boundaries has been proven a prominent way to enhance the performance of grain boundaries in many material systems, including ceramics and alloys [13-17], the interactions between solute atoms and grain boundaries in ZrB_2 have not been investigated until now. The present work deals with segregations of solute atoms in ZrB_2 grain boundaries and their influences on grain boundary strengths by first-principles calculation based on density functional theory, while it has been proved as a powerful method to evaluate the energetics, chemical or bonding state of grain boundaries [13-16]. Since the solute atoms usually result from diffusion of elements from additives or second phases into ZrB_2 during sintering, the selected solute atoms include Y, Nb, Ta, Mo and W, as guided by additives or second phases (e.g., Y_2O_3 , TaSi_2 , MoSi_2 , WSi_2 or WC) commonly added into ZrB_2 . The results are not only useful in understanding the outstanding high temperature performance of ZrB_2 ceramics with additives of TaSi_2 , MoSi_2 , WSi_2 or WC , but also valuable for further design of UHTCs.

2. Computational details

First-principles simulations were performed by using CASTEP [18] with exchange-correlation described by generalized gradient approximation [19]. In the simulations, Vanderbilt-type ultrasoft pseudopotential [20] was employed with cutoff energy of the plane wave being 400eV. k -points mesh with separation of $0.04\text{\AA}^{-1}$ was sampled according to Monkhorst-Pack method [21] in the Brillouin zone. All of the supercells containing grain boundaries were fully optimized with respect to both lattice parameters and atom positions by using Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization scheme [22]. The tolerances for geometry optimization were set as follows: difference in total energy within $5\times 10^{-6}\text{eV/atom}$, maximum ionic Hellmann-Feynman force within $0.01\text{eV/\AA}$, maximum ionic displacement within $5\times 10^{-4}\text{\AA}$ and maximum stress within 0.02GPa.

To assess the effects of solute atom segregation on grain boundary strengths, tensile stress-strain relations of grain boundaries were simulated. During the simulation, the supercell was incrementally deformed in the imposed strain direction. At each step, the supercell was fully relaxed by employing BFGS minimization scheme until all other stress components vanished. Then, the relaxed supercell was taken as the starting structure for the next step to ensure the stress-strain curves being continuous.

3. Structural models of grain boundaries

Selection of grain boundaries was guided by coincident site lattice (CSL) theory [16, 23]. Three symmetrical tilt grain boundaries with their rotation axis respectively

being [0001], [1120]/3 and [0110] of ZrB_2 were selected. The CSL structure of each boundary is respectively shown in Fig. 1a-1c with the corresponding atomic structure demonstrated in Fig. 1d-1f. As illustrated in Fig. 1a, when two crystals are at a specific orientation relationship, a portion of lattice points from either lattice are coincident with each other (big, black points in Fig. 1a). Such a coincident lattice point is called a coincident site. Due to the periodic nature of both crystals, the coincident sites sometimes also form a periodic lattice (Fig. 1a), which is called CSL. In principle, exact CSL orientation relationship can only be defined by rotations around the c -axis for hexagonal crystals with irrational c^2/a^2 [16, 23]. Nevertheless, near CSL structure can still be obtained for rotation axis other than c -axis. At this circumstance, small elastic constraints should be introduced into the system to define a constrained CSL [24]. When a CSL is defined, a supercell of the CSL can be selected to model a grain boundary. The box encircled by red and blue lines in Fig. 1a demonstrates the supercell selected to model a grain boundary. The black line represents the grain boundary position. The red crystal is located in the region enclosed by the red lines and the black line, while the blue crystal is located in the region enclosed by the blue lines and the black line. The advantage of selecting a CSL supercell to model a grain boundary is that the system naturally meets periodic boundary condition, since only periodic supercells are admissible in CASTEP. Therefore, each supercell contains two grain boundaries due to the periodic boundary condition, as demonstrated in Fig. 1d-1f.

[Fig. 1]

For a CSL, volume ratio between the primitive cell of the CSL to that of the crystal is defined as Σ value of the CSL [16, 23]. Then, Σ values for boundaries in Fig. 1a-1c are 7, 8 and 6, respectively. These grain boundaries will be called $\Sigma 7$, $\Sigma 8$, and $\Sigma 6$ boundary for simplicity. For the $\Sigma 7$ grain boundary, the boron-net keeps planar, which is interconnected by a sequence of 5-membered and 7-membered rings across the grain boundary, as illustrated in Fig. 1d. For the $\Sigma 8$ grain boundary, the boron-net is interconnected by 8-membered rings with a shift between the 8-membered rings in adjacent layers, as demonstrated in the extracted boundary 3D structure in Fig. 1g. For the $\Sigma 6$ grain boundary, the boron-net is interconnected by alternatively appeared 4-membered and 8-membered rings, as shown in Fig. 1h. Similar to the $\Sigma 8$ grain boundary, the boron rings in the $\Sigma 6$ grain boundary also displays a relative shift between adjacent boron layers. The tilt angles, number of ZrB_2 cells (N), number of B atoms (N_B) and Zr atoms (N_{Zr}), grain boundary orientations and basis vectors of the supercells (a , b and c) in either crystal are listed in Table 1. In principle, the number of ZrB_2 cells for each crystal combining the grain boundary should be an integral multiple of the Σ value. However, when a boundary is constructed, some atoms may locate too close to each other, which should be deleted. As a consequence, it can be deduced from Table 1 that one Zr and two B of each crystal were deleted in the $\Sigma 7$ boundary supercell and one B of each crystal was deleted in the $\Sigma 8$ boundary supercell. For more details, please refer to the supplementary material.

[Table 1]

4. Results and discussions

4.1. Grain boundary energies

The supercells were first optimized with respect to both lattice parameters and atom positions by using the BFGS minimization scheme. Lattice parameters of the supercells before and after geometrical optimization are listed in Table 2. There is no significant change in lattice parameters after optimization, which means that the adopted grain boundary models are stable. Lattice parameters with and without optimization can be adopted to estimate the elastic energy:

$$E_{\text{elastic}} = \frac{1}{2} C_{ijkl} \varepsilon_{ij} \varepsilon_{kl} V \quad (1)$$

where Einstein's notation over repeated indices is used, C_{ijkl} is the fourth order elastic tensor of ZrB_2 , ε_{ij} is the elastic strain, V is the volume of the supercell. The elastic strain tensor can be calculated as:

$$\varepsilon_{ij} = \frac{1}{2} (F_{ij} + F_{ji}) - \delta_{ij} \quad (2)$$

where the deformation gradient matrix $\mathbf{F}$ connects a vector before and after optimization as:

$$\mathbf{x}_{\text{after}} = \mathbf{F} \mathbf{x}_{\text{before}} \quad (3)$$

With the lattice parameters in Table 2 and lattice directions in Table 1, the elastic energy for each supercell can be calculated, and the results are listed in Table 3. The elastic constants used in the current work are $C_{11}=C_{22}=566.4\text{GPa}$, $C_{33}=433.2\text{GPa}$,

$C_{44}=253.5\text{GPa}$, $C_{66}=258.0\text{GPa}$, $C_{12}=50.4\text{GPa}$, $C_{13}=C_{23}=121.8\text{GPa}$, which are consistent with values reported by others [25-27]. The transformation between the matrix form C_{IJ} and fourth order tensor notation C_{ijkl} of elastic constants and coordination transformation of tensors can be found in Reference [28].

Grain boundary energy γ can be evaluated as:

$$\gamma = \frac{E_{\text{sc}} - nE_{\text{bulk}} - E_{\text{elastic}}}{2A} \quad (4)$$

where E_{sc} is the total energy of the supercell that contains two grain boundaries; n is the number of ZrB_2 unit cells in the supercell. E_{bulk} is the total energy of a ZrB_2 unit cell. A is the area of the grain boundary. The values of $E_{\text{sc}} - nE_{\text{bulk}}$, A , and γ are also listed in Table 3. As shown in the table, elastic energies in these systems are negligible in comparison to $E_{\text{sc}} - nE_{\text{bulk}}$, which means that the simulation systems are almost free from influence of elastic deformations since the supercells meet the CSL or near CSL condition. Our calculated interfacial energy of the $\Sigma 7$ grain boundary agrees well with the value computed by Lawson *et al* [29], demonstrating the reliability of our calculations. Interfacial energy of the $\Sigma 8$ grain boundary cannot be obtained because of the deviation of Zr/B ratio from the stoichiometry of ZrB_2 . Then, only a possible range is provided in Table 3. Discussion on its possible range is in the supplementary material.

[Table 3]

4.2. Segregation of solute atoms

There are two characteristic sites in the $\Sigma 7$ boundary, which will be referred to as 5-5 site and 7-7 site for simplicity. The 5-5 site means that the metal atom is bonding with 5 and 5 B atoms in the adjacent boron layers. In analogous, grain boundary site for the $\Sigma 8$ and $\Sigma 6$ boundary are 1-8 site and 4-8 site, respectively. To evaluate the segregation tendency of a solute atom, the solute atom is inserted into ZrB_2 grains or the characteristic sites of a boundary. Taking the $\Sigma 7$ boundary for example, the solute atom is either inserted into site 1 and 1' or site 2 and 2', as demonstrated in Fig. 2. Then, energy difference between these two configurations $\Delta_{5-5} = (E_{22'} - E_{11'})/2$ indicates the segregation tendency of the solute atom into the 5-5 site. A negative segregation energy Δ_{5-5} means the solute atom tends to segregate into 5-5 site of the boundary. The lower Δ_{5-5} is, the stronger the segregation tendency is. Δ values corresponding to the four characteristic boundary sites are listed in Table 4. The results reveal that Y tends to segregate into 7-7 sites of the $\Sigma 7$ boundary and the $\Sigma 6$ boundary, while Nb, Ta, Mo or W tends to segregate into 5-5 sites of the $\Sigma 7$ boundary and the $\Sigma 8$ boundary.

[Figure 2]

[Table 4]

The segregation tendency exhibits two special characteristics. First, the segregation energies of Nb and Ta (or Mo and W) are similar to each other, which may result from the similarities in their electronic structure and atom radius. Second,

Y displays opposite segregation tendency in comparison with Nb, Ta, Mo or W. The opposite segregation tendency is found correlated to the local bond length between metal atom and B (M-B bond). The average M-B length of 5-5, 7-7, 1-8 and 4-8 site is respectively 2.387Å, 2.759Å, 2.439Å and 2.589Å. It implies that Y tends to segregate into site with long M-B bonds, while Nb, Ta, Mo or W tends to segregate into site with short M-B bonds. The tendency is consistent with the fact that the M-B bond length of YB₂ is larger than that of ZrB₂, while the M-B bond length of NbB₂, TaB₂, MoB₂ or WB₂ is shorter than that of ZrB₂ [25, 27]. The equilibrium Zr-B length 2.544Å can be taken as a rough boundary to distinguish whether a site is preferred by Y or by Nb, Ta, Mo or W.

4.3. Grain boundary strength

To assess the influences of solute atoms on grain boundary strengths, tensile stress-strain curves of grain boundaries with the grain boundary sites occupied by different solute atoms were simulated, as shown in Fig. 3. In principle, the solute atoms were introduced as columns due to the periodic repetition of supercell. Such a 2D periodic occupation of solute atoms at grain boundary were frequently observed in experiments [13-15, 17], which are called “grain boundary complexions” by some investigators [17]. It means that our simulations are close representations of real grain boundaries when solute atoms tend to segregate into grain boundaries. For each grain boundary, tensile stress-strain curve of the boundary without any solute atom and tensile stress-strain curve of bulk ZrB₂ normal to the boundary plane were simulated

for comparison. As can be seen from the figures, solute atoms change the stress-strain responses of grain boundaries remarkably, indicating the strong influences of solute atoms on grain boundary properties.

[Figure 3]

[Table 5]

Table 5 lists the simulated tensile strength values. Similar to the segregation tendency, influences on grain boundary strengths are similar for Nb, Ta, Mo or W, which is different from those of Y. Occupying all the characteristic grain boundary sites by Y displays no evident improvement on grain boundary strength. Instead, a substantial decrease in the strength of the $\Sigma 6$ boundary due to preferential segregation of Y is obtained, which means that Y serves as a poison to the $\Sigma 6$ boundary. Due to the long equilibrium Y-B bond length, segregation of Y will result in local expansions around grain boundaries, which will possibly reduce the strength of grain boundaries. As illustrated in Fig. 4, the bond connecting B₃ and B₄, which is under tension during the tensile deformation, expands from 1.778Å to 1.854Å for Y segregation. The expansion of B₃-B₄ bond reduces its bonding strength, as can be inferred from the electron density difference map in Fig. 4, wherein the enrichment of valence electrons between B₃ and B₄ due to chemical bonding decreases for Y segregation. It indicates that the poisoning effect of Y segregation on grain boundary properties may result from the local expansions around grain boundaries. Such a poisoning effect will

deteriorate the performance of materials. Accordingly, it is better to avoid adding additives containing Y, e.g. Y_2O_3 , in manufacturing ZrB_2 based UHTCs.

[Figure 4]

For Nb, Ta, Mo or W, remarkable improvement on grain boundary strength is obtained when the solute atom prefers to segregate into the grain boundary site. Particularly, the strength of the $\Sigma 8$ boundary with segregation of Mo or W is comparable to the strength of bulk ZrB_2 . Instead of local expansions, segregation of Nb, Ta, Mo or W into grain boundaries will result in local contractions around grain boundaries due to the short equilibrium M-B (M = Nb, Ta, Mo or W) bonds. For example, the length of B-B_{inter} bond (inset of Fig. 5) in the $\Sigma 8$ boundary reduces from 1.960Å to 1.853Å due to the segregation of Mo. Fig. 5 shows the elongation-strain curves of B-B_{inter} and B-B_{intra} bonds with and without Mo segregation for the $\Sigma 8$ boundary. It is clear that the elongation-strain response of the B-B_{inter} bond is significantly affected due to the segregation of Mo, while no evident change in the response of the B-B_{intra} bond is obtained. Interestingly, Fig. 5 also demonstrates that preferential elongation of the B-B_{intra} bond happens with the segregation of Mo, which is consistent with the result that the strength of supercell is comparable to that of ZrB_2 crystal. The local contraction effect induced by segregation of Nb, Ta, Mo or W might be the origin of the enhanced performance of grain boundaries. Though the boundary strength will be reduced when Nb, Ta, Mo or W occupies an energetically unfavorable

grain boundary site, except that occupying the grain boundary by Nb or Ta displays no harm to the $\Sigma 6$ boundary, the overall effect of Nb, Ta, Mo or W is believed to strengthen grain boundaries, since the unfavorable occupation can be avoided by annealing treatment.

[Figure 5]

Combining the calculated segregation energies and grain boundary strengths, the influence of solute atoms on grain boundaries are summarized in Fig. 6. For simplification, Fig. 6 is divided into five specific regions, as demonstrated by different colors. The figure can be used as a reference for the selection of solute atoms to enhance the performance of grain boundaries. The best way is to search for elements located in the green region, where solute atom exhibits strong segregation tendency and improves the grain boundary properties remarkably. In addition to the strengthening effect, solute atom segregation also exhibits pinning effect on grain boundaries [16]. The lower the negative segregation energy Δ is, the higher the pinning effect is. Therefore, Nb, Ta, Mo or W will display strong pinning effect on the $\Sigma 7$ and $\Sigma 8$ boundaries. The pinning effect on grain boundaries can suppress grain growth during manufacturing ZrB_2 based UHTCs, which will result in a uniform fine-sized microstructure that exhibits excellent mechanical properties. Moreover, suppressing grain growth during service at high temperatures can also increase the performance of ZrB_2 based UHTCs, since extremely large ZrB_2 grains resulting from

abnormal grain growth usually serve as nucleation positions for cracks [30]. Due to the diversity of grain boundaries, solute atom interacts differently with different grain boundaries. The interaction between an element and grain boundaries cannot all locate in the green region. If the point representing the interaction between the element and a boundary locates in the region colored by light gray, the interaction can be neglected during the analysis, since the grain boundary will almost be free of the solute atom at this circumstance. Cautions should be exercised for points dropped in the red region, which may induce weak boundaries by solute atom segregation as nucleation sites for micro-cracks. Therefore, elements with points dropped in the red region should be avoided during materials design. The two shape regions in the middle of Fig. 6 mean that neither segregation or depletion tendency of solute atom is strong, the solute atom concentration at grain boundaries may comparable to that of the grains, especially when materials serve at evaluated temperature. For example, the interaction between Nb, Ta, Mo or W and the $\Sigma 6$ boundary locates close to these regions. The strength of the $\Sigma 6$ boundary will decrease with the increase of the concentration of Mo or W. Nevertheless, the reduction in grain boundary strength is minor in real materials because of low solute atom concentration, e.g. 2 at.% W in ZrB_2 as reported by Silvestroni and Sciti [11].

In our previous work [31], we have proved that solid solution of Nb, Ta, Mo or W into ZrB_2 can reduce the critical stress for dislocation nucleation, which will in turn increase the damage tolerance of ZrB_2 grains. In combination with strengthening and pinning effect of Nb, Ta, Mo or W on ZrB_2 grain boundaries, ZrB_2 based UHTCs with

additives containing Nb, Ta, Mo or W elements will result in a uniform fine-sized microstructure with strong grain boundaries and damage tolerance grains, which is believed responsible for the outstanding high temperature mechanical properties. Nowadays, Nb, Ta, Mo or W is usually added in the form of metal disilicide (MSi_2) [4, 9-11]. Unfortunately, the use of ZrB_2 based UHTCs with MSi_2 additives in the ultra-high temperature regimes is restricted by the low melting temperatures of MSi_2 s, even though they display outstanding high temperature properties. These mechanisms due to solid solution are significant in the design of ZrB_2 based UHTCs. For example, $(\text{Zr,M})\text{B}_2$ ($\text{M} = \text{Nb, Ta, Mo or W}$) based UHTCs with reducing additives to remove surface oxides and enhance densification may be suitable for the use in the ultra-high temperature regimes, since the shortcoming due to low melting temperature of MSi_2 is overcome.

5. Summary

The segregation tendency of Y, Nb, Ta, Mo and W in ZrB_2 grain boundaries and the effects of solute atom segregation on grain boundary strengths have been investigated by first-principles calculations. In the study, three symmetrical tilt grain boundaries with their rotation axis respectively being $[0001]$ (the $\Sigma 7$ boundary), $[1120]/3$ (the $\Sigma 8$ boundary) and $[0110]$ (the $\Sigma 6$ boundary) have been selected.

The results reveal that Y displays opposite segregation tendency in comparison with Nb, Ta, Mo or W, i.e., Y tends to segregate into site with long M-B bonds, while Nb, Ta, Mo or W tends to segregate into site with short M-B bonds. The equilibrium

Zr-B bond length in ZrB_2 is suggested as a rough boundary to distinguish whether a site is preferred by Y or by Nb, Ta, Mo or W. Studies on grain boundary strengths indicate that segregation of Y exhibits softening effect on grain boundaries, which may result from local expansions due to the long Y-B bonds. Accordingly, additives with Y should be avoided in the manufacture of ZrB_2 based UHTCs. In contrast, segregation of Nb, Ta, Mo or W into grain boundaries can increase grain boundary strengths remarkably by introducing local contractions induced by the short M-B (M = Nb, Ta, Mo or W) bonds around grain boundaries. Both strengthening and pinning effect due to segregation of Nb, Ta, Mo or W are believed to contribute to the outstanding high temperature properties of ZrB_2 based UHTCs with additives of compounds containing Nb, Ta, Mo or W.

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Table 1. Basic information on the supercells of the $\Sigma 7$, $\Sigma 8$ and $\Sigma 6$ boundaries, including the tilt angle of each crystal, number of ZrB_2 cells (N), number of B atoms (N_B) and Zr atoms (N_{Zr}), interface orientation and a , b , c vector of the supercells expressed in either side of crystal. C_r and C_b represent crystal red and blue in Fig. 1, respectively.

Table 2. Lattice parameters of supercells before and after optimization.

Table 3. Interfacial energy (γ), exceeding energy ($E_{\text{sc}} - nE_{\text{bulk}}$), elastic energy (E_{elastic}) and interface area (A) of the $\Sigma 7$, $\Sigma 8$ and $\Sigma 6$ boundaries.

Table 4. Energy differences (in eV) between the configurations of solute atom segregated in the boundary site and located in the ZrB_2 crystal. Data in parentheses represent the changes of grain boundary energies (in $\text{meV}/\text{\AA}^2$) when all the characteristic sites are occupied.

Table 5. Tensile strength (in GPa) of grain boundaries with different solute atoms. Values labeled “Bulk” represent tensile strength of bulk ZrB_2 normal to grain boundary planes. The underlined values mean that occupying the site by the solute atom is energetically unfavorable. Data in parentheses represent the relative changes ($\tau_X/\tau_{\text{Zr}} - 1$, in %) of grain boundary strengths.

Figure 1. (a)-(c) respectively demonstrates coincident site lattice (CSL) structure for ZrB_2 with rotation axis being $[0001]$ ($\Sigma 7$), $[1120]/3$ ($\Sigma 8$) and $[0110]$ ($\Sigma 6$). Red and blue points are lattice points prior to and after rotation, while black points are coincident sites. Boxes encircled by red and blue lines are systems selected to model grain boundaries with black lines being grain boundaries. (d)-(f) represent atomic configurations in accordance with (a)-(c), respectively. Atoms surrounding grain boundaries are highlighted by different colors. (g) is the extracted 3D atomic structure around the boundary in (e), while (h) is the extracted 3D atomic structure around the boundary in (f). Arrows in (g) and (h) illustrate the view direction (tilt axis direction) in (e) $[1120]/3$ and (f) $[0110]$, respectively. More information can be found from 3D figures in the supplementary material.

Figure 2. Illustration of inserting solute atom into ZrB_2 grains (site 1 and 1') or into grain boundaries (2 and 2' represent the 5-5 sites, 3 and 3' represent the 7-7 sites).

Figure 3. Stress-strain curves of interfaces with different solute atoms: (a) the $\Sigma 7$ boundary with the 5-5 site filled by different solute atoms, (b) the $\Sigma 7$ boundary with the 7-7 site filled by different solute atoms, (c) the $\Sigma 8$ boundary filled by different solute atoms, and (d) the $\Sigma 6$ boundary filled by different solute atoms. In the figures, curves with solid points mean that the solute atoms tend to segregate into the site, while curves with hollow points mean that occupying the sites by the solute atoms is energetically unfavorable. Lines labeled “Bulk” represent tensile stress-strain curves

of bulk ZrB_2 normal to the corresponding grain boundary plane.

Figure 4. Electron density difference map of the $\Sigma 6$ boundary occupied by (a) Y and (b) Zr. The map plane passes through the quadrilateral B nets of the boundary.

Figure 5. Elongation-strain curves of the $\text{B-B}_{\text{inter}}$ and $\text{B-B}_{\text{intra}}$ bonds of the $\Sigma 8$ boundary with (solid points with solid lines) and without (hollow points with dash lines) segregation of Mo. Inset illustrates the $\text{B-B}_{\text{inter}}$ and $\text{B-B}_{\text{intra}}$ bonds.

Figure 6. Illustration of the influences of solute atoms on grain boundaries. Values in parentheses in Table 4 and Table 5 are used in the plot.

Figure1

Figure2

Figure3

Figure4

Figure 5

Figure6

Table 1. Basic information on the supercells of the $\Sigma 7$, $\Sigma 8$ and $\Sigma 6$ boundaries, including the tilt angle of each crystal, number of ZrB_2 cells (N), number of B atoms (N_B) and Zr atoms (N_{Zr}), interface orientation and a , b , c vector of the supercells expressed in either side of crystal. C_r and C_b represent crystal red and blue in Fig. 1, respectively.

		Tilt angle	N	N_B	N_{Zr}	Interface orientation	a	b	c
$\Sigma 7$	C_r	79.11°	13	26	13	(2130)	[2130]	[0001]	[4510]/3
	C_b	-79.11°	13	26	13	(1230)	[1230]	[0001]	[5410]/3
$\Sigma 8$	C_r	40.89°	8	15	8	(1101)	[7819]/3	[1213]/3	[2113]/3
	C_b	-40.89°	8	15	8	(1101)	[7819]/3	[2113]/3	[1213]/3
$\Sigma 6$	C_r	37.78°	12	24	12	(2111)	[10556]/3	[1213]/3	[1123]/3
	C_b	-37.78°	12	24	12	(2111)	[10556]/3	[1213]/3	[1123]/3

Table 2. Lattice parameters of supercells before and after optimization.

		a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
$\Sigma 7$	before	26.964	3.536	8.382	90	90	90
	after	27.103	3.556	8.422	90	90	90
$\Sigma 8$	before	34.828	4.748	4.748	39.98	90	90
	after	33.941	4.762	4.762	39.16	90	90
$\Sigma 6$	before	34.696	4.748	4.748	70.61	90	90
	after	35.054	4.743	4.743	70.87	90	90

Table 3. Interfacial energy (γ), exceeding energy ($E_{\text{sc}} - nE_{\text{bulk}}$), elastic energy (E_{elastic}) and interface area (A) of the $\Sigma 7$, $\Sigma 8$ and $\Sigma 6$ boundaries.

	$E_{\text{sc}} - nE_{\text{bulk}}$ (meV)	E_{elastic} (meV)	A ($\text{\AA}^2$)	γ (meV/ $\text{\AA}^2$)
$\Sigma 7$	9612.5	147	29.95	157
$\Sigma 8$	-	67	14.32	84~155
$\Sigma 6$	5268.7	153	21.26	120

Table 4. Energy differences (in eV) between the configurations of solute atom segregated in the boundary site and located in the ZrB_2 crystal. Data in parentheses represent the changes of grain boundary energies (in meV/ $\text{\AA}^2$) when all the characteristic sites are occupied.

		Y	Nb	Ta	Mo	W
$\Sigma 7$	Δ_{5-5}	1.85 (61.8)	-1.49 (-49.7)	-1.36 (-45.4)	-2.95 (-98.5)	-2.97 (-99.2)
	Δ_{7-7}	-1.19 (-39.7)	1.16 (38.7)	1.18 (39.4)	1.88 (62.8)	2.08 (69.4)
$\Sigma 8$	Δ_{1-8}	0.54 (37.7)	-1.42 (-99.2)	-1.48 (-103.4)	-2.59 (-180.9)	-2.77 (-193.4)
$\Sigma 6$	Δ_{4-8}	-0.71 (-33.4)	0.13 (6.1)	0.10 (4.7)	0.20 (9.4)	0.23 (10.8)

Table 5. Tensile strength (in GPa) of grain boundaries with different solute atoms.

Values labeled “Bulk” represent tensile strength of bulk ZrB_2 normal to grain boundary planes. The underlined values mean that occupying the site by the solute atom is energetically unfavorable. Data in parentheses represent the relative changes ($\tau_X/\tau_{\text{Zr}} - 1$, in %) of grain boundary strengths.

		Bulk	Zr	Y	Nb	Ta	Mo	W
$\Sigma 7$	5-5	36.4	27.9	<u>15.8</u> (-43.4)	31.7 (13.6)	31.4 (12.5)	32.0 (14.7)	31.8 (14.0)
	7-7	36.4	27.9	28.3 (1.4)	<u>20.9</u> (-25.1)	<u>15.5</u> (-44.4)	<u>20.1</u> (-28.0)	<u>10.3</u> (-63.1)
$\Sigma 8$	1-8	45.5	31.8	<u>13.6</u> (-57.2)	42.1 (32.4)	42.7 (34.3)	46.1 (45.0)	46.1 (45.0)
$\Sigma 6$	4-8	55.6	37.9	20.9 (-44.9)	<u>38.9</u> (2.6)	<u>37.7</u> (-0.5)	<u>29.1</u> (-23.2)	<u>29.5</u> (-22.2)

symmetrical tilt grain boundary of ZrB_2 with rotation axis:
 (a) $[0001]$ ($\Sigma 7$) (b) $[11\bar{2}0]/3$ ($\Sigma 8$) (c) $[01\bar{1}0]$ ($\Sigma 6$)
 Nb, Ta, Mo or W tends to segregate into sites encircled in red
 Y tends to segregate into sites encircled in blue