Supporting Online Material

Materials and methods

The binding energy per one sulfur atom in the GB with respect to the atomic gas state of sulfur, \(-E^GB_b\), is calculated as follows.

\[
E^GB_bN_S = E^GB_{tot}(N_{Ni},N_S) - N_SE^\text{atom,S}_{tot} - E^GB_{tot}(N^0_{Ni}) - \frac{N_{Ni} - N^0_{Ni}}{N^0_{Ni}}E^\text{Bulk}_{tot}(N^0_{Ni})
\]

Here, \(E^GB_{tot}(N_{Ni},N_S)\) indicates the calculated total energy of the GB unit cell that includes \(N_{Ni}\) nickel atoms and \(N_S\) sulfur atoms, \(E^\text{atom,S}_{tot}\) the total energy of one isolated sulfur atom, \(N^0_{Ni}\) number of nickel atom in clean GB and bulk unit cells. The last term is to adjust the number of nickel atoms when sulfur atoms are substituted for nickel atoms. The total energy of an isolated sulfur atom is calculated using a large super cell (10x10x10 in Å) with spin polarization and symmetry breaking according to the VASP manual. The binding energy of sulfur atom in bulk unit cell can be calculated in a similar manner.

In the total energy calculations, the length of \(c\) axis is optimized by polynomial fitting of several calculated total energies, in which each total energy is obtained after atomic geometry optimization by force minimization procedure at fixed \(c\)-axis length. The final total energy is calculated under the optimized length of \(c\) axis with atomic geometry relaxation.

Since the sulfur segregation occurs only at two or three layers in twenty nickel layers of this unit cell, the lengths of \(a\) and \(b\) axes are fixed. The lengths of \(a\) and \(b\) axes are determined by the optimization using bulk unit cell that is explained in text. We do not take into account the effect of the GB shift (sliding) in the \(ab\) plane. Since the atomic geometry optimization and \(c\)-axis optimization is necessary for each single shift to find the energy minimum point, it is too time-consuming for us to perform. In addition, the segregation points may change after shifting.
The cutoff energy for the plane wave basis set is 280 eV. The k-point mesh is $2 \times 2 \times 1$. The Methfessel-Paxton smearing method with 0.1-eV smearing width is used. All calculations are done in non-magnetic state to save computational time. In our previous works ($S1, S2$), we checked that the magnetism of nickel does not influence appreciably on the calculated binding energy and segregation energy.

The detail information of the input files we used are as follows.

**INCAR file:**

```
PREC = Normal; ISYM = 0; ISPIN = 1
EDIFF = 0.0005; EDIFFG = -0.05
ISMEAR = 1; SIGMA = 0.10
AMIX = 0.02; BMIX = 0.0001; LREAL = .FALSE.
ENCUT = 280.000; ENAUG = 544.565
IBRION = 1; ISIF = 2; POTIM = 0.5
```

**KPOINTS file:**

```
Auto
0
Monkhorst Pack
2 2 1
0 0 0
```

**POTCAR file:**

```
PAW_PBE Ni 06Sep2000
PAW_PBE S 17Jan2003
```

**POSCAR file:**

```
# The optimized Sigma5(012) grain boundary structure
1.0000000000000000
 7.0400000000000000 0.0000000000000000 0.0000000000000000
0.0000000000000000 7.8709600000000000 0.0000000000000000
0.0000000000000000 0.0000000000000000 16.3606000000000000
80
Selective dynamics
Direct
-0.0000006103273471 1.0032983828116630 0.0000345492239317 T T T
0.2499934899208866 0.5033169937303336 0.0000365610618833 T T T
0.499991033842533 1.0032912993671960 0.0000325439771300 T T T
0.7500059702303761 0.5033210535115078 0.0000392029465182 T T T
1.0000004843823010 0.6979889491195963 0.0671671996191150 T T T
0.2499968375810694 0.1980225342070272 0.0671727290422612 T T T
```
For some cases, the calculated results from VASP are confirmed to agree with those from WIEN2k (S3), which is based on the most accurate band structure calculation method called full-potential linearized augmented plane wave method (S4). Using a smaller unit cell that contains about 20 atoms, the binding energies of sulfur atom calculated by VASP/WIEN2k at FS0, GB0, GB1, and GB6 sites are 5.71/5.94, 4.70/4.91, 3.30/3.46, and 2.85/3.04 (eV/S), respectively.

Supporting online text (SOM text)

(a) $\Sigma 5(012)$ symmetrical tilt grain boundary

There are two reasons to chose this $\Sigma 5(012)$ symmetrical tilt GB for our calculations. First, a stable adsorption site on a (012) free surface for sulfur atom (FS0 site) does not neighbor with each other and its area density is $7.22 \times 10^{14}$ (atoms/cm$^{-2}$), which is
very close to the experimentally determined maximum number of sulfur atoms adsorbed on a (012) surface, \(7.9 \times 10^{14} \text{ (atoms/cm}^{-2}\text{)}(S5)\). Second, the GB energy is moderate, which is important for self-consistent calculation and geometry optimization by force minimization. Some high energy GBs like \(\Sigma 7\) are so unstable that the calculations are difficult to converge in our experience. The calculated GB energy for a \(\Sigma 5(012)\) GB is \(1.19 \text{ (J/m}^2\text{)}\), which is about half of a (012) free surface (FS) energy, \(2.40 \text{ (J/m}^2\text{)}\). Here, GB/FS energy is calculated as a difference in the total energies between the GB/FS unit cell and the Bulk unit cell, in which the size of the unit cells for the three cases are chosen to be almost the same in order to calculate the accurate total energy difference among the three unit cells. In our previous works (1,2), we show the interlayer distances for the GB and FS unit cells.

When we calculate surface adsorption energy of sulfur, we use a unit cell in which a half of crystal (from GB-2 to GB-10 in Fig. 1A) in GB unit cell is replaced by vacuum region. Since we took a large size of two dimensional unit cell in \(ab\)-plane, four FS0 sites are included on the surface. The binding energy (adsorption energy) of one sulfur atom at one FS0 site is \(6.06 \text{ eV/S}\), which does not change appreciably from the average value, \(5.80 \text{ (eV/S)}\), when four sulfur atoms are placed at four FS0 sites. This is consistent with the experimental fact that the area density of sulfur atoms in this case is close to but under the experimental maximum density of adsorbed sulfur atoms as stated above.

(b) Segregation free energy in McLean’s equation

McLean (S6) modeled solute (impurity) segregation to GBs by considering two semi-infinite crystals with a uniform solute segregation, and he described diffusion in these two crystals using Fick’s laws. In addition, two initial assumptions about the GB are made; (i) that the GB has a finite width and (ii) that the GB contains a finite number
of segregation sites that have a fixed segregation free energy. Also, McLean assumed that the chemical potential of the solute was different inside and outside the GB with a discontinuity existing at the interface. From this initial set up, McLean derived the temperature dependence of GB segregation as shown in the main text.

Strictly speaking, the segregation energy $\Delta E_{\text{seg}}$ in the main text should be the difference in Gibbs free energies ($\Delta G = \Delta U + \Delta(pV) - T\Delta S$) between GB/FS and Bulk unit cells. Here, we can neglect the $pV$ term since the difference in this term is thought to be negligible under unstressed conditions. The entropy term is roughly estimated by Rice and Wang\(^{(S7)}\) to be positive about $\Delta S = 0.0-0.03$ (kJ/mol) from various experiments. According to their estimation, the free energy of segregation, $-\Delta G$, is larger by about 0.0-0.3 eV/S at 1000 K than the energy (or enthalpy) of segregation, $-\Delta E_{\text{seg}}$.

(c) **The depth dependence of the concentration**

The distances from the GB0(GB1) plane for sulfur atoms at GB2, GB3, GB4, GB5, and GB6 sites are 1.32, 1.64, 2.01, 3.59, and 4.12 Å, respectively. As stated in the main text, the occupations for GB0 and GB2 sites are almost 1.0 while that for the other sites are under 0.1. Roughly speaking, the above site occupations are consistent with the depth dependence of the concentration of segregant from the GB plane that is experimentally observed by the Auger electron spectroscopy analysis\(^{(S8)}\). The observed depth dependence shows an exponential decrease in which the occupation at the 5 Å depth from the GB plane is only about 20% of that at just the GB plane.

(d) **Interaction energies among segregated sulfur atoms**

The total energy loss due to an interaction among the eight sulfur atoms at four GB0 and four GB2 sites can be estimated to be (4.75×4+4.66×4−4.23×8=) 3.8 eV. In text, we discuss only the average binding energy for all sulfur atoms. It means that the total
interaction energy between sulfur atoms is assumed to be equally distributed to them. However, it is not correct if the GB2 sites are not fully occupied by sulfur. As shown in Fig. 1B, one sulfur atom at one GB2 site neighbors only two sulfur atoms at GB0 sites. The other two GB0 sites are relatively far. Therefore, if one sulfur atom is substituted for nickel atom at one GB2 site after four GB0 sites are occupied by sulfur, the interaction energy between sulfur atoms should be mainly distributed only to the neighboring three sulfur atoms.

In this case, the average binding energy decreases from 4.75 eV/S to 4.49 eV/S as shown in table 1, although the binding energy when only one sulfur atom is placed at the GB2 site is 4.67 eV/S. From these values, the energy loss by adding one sulfur atom at GB2 site is estimated to be \((4.75 \times 4 + 4.67 - 4.49 \times 5) = 1.22\) eV. Since the binding energies of GB0 and GB2 are almost the same when there is no interaction between them, we think that this energy loss (1.22 eV) is equally distributed to three sulfur atoms at one GB2 site and two GB0 sites. The average binding energy for the three sulfur atoms is estimated to be \((4.75 \times 2 + 4.67 - 1.22)/3 = 4.32\) eV/S, which is still enough large for high occupation as in Fig. 2A.

(e) Comparison of the segregation energies between theory and experiment

We can compare the calculated segregation energy with the experiment. The difference in the binding energies between GB sites and inner bulk sites is segregation energy. In the main text, the average binding energy vary from 4.75 to 3.85 eV/S depending on the occupation of sulfur atoms in the GB region. From these results about the binding energies, the average segregation energy vary from 1.79 eV/S to 0.88 eV/S. As stated in (b), the contribution of the entropy term is thought to be small.

Experimentally, the segregation free energy of sulfur to the GBs was estimated to be
98 \text{ kJ/mol (1.02 eV/S)} \text{ (S9)}, which is in the same order of magnitude with our calculated results. It should be noted here that this experimental estimation is based on the analysis for the temperature dependence of the concentration of segregant in the GB region using McLean’s equation. For this reason, the obtained experimental segregation free energy is an average value on various kinds of GB and various segregation sites that are not known precisely. In addition, the interaction among segregants is not taken into account.

\textbf{(f) The expansion of bond length in the GB expansion}

We illustrate that the atomic “size effect” is not a sufficient concept in this case.

Table S1 shows the bonding lengths of Ni-Ni and Ni-S when the GB0 sites are fully occupied by sulfur. From this table, we can see that the Ni-S distance is about 2.27Å. For fcc Ni, the nearest neighbor distance of Ni is 2.49Å. From these two lengths, we can obtain that the atomic radii of Ni and S atoms in this case are 1.25 and 1.03 Å, respectively. The radius of S is 1.03 Å, which is comparable to the radius estimated from the S-S distance (1.9Å) of S\textsubscript{2} molecule.

Table S2 shows the bonding lengths after all Ni atoms at GB2 sites are replaced by S atoms in addition to GB0 sites. The S(GB0)-Ni(GB-2) and S(GB0)-Ni(GB-3) distances are still about 2.27Å. However, we can see that S(GB0)-S(GB2) distance is 3.3Å, which is very long comparing with S(GB0)-Ni(GB2) distance (2.27Å) in Table S1. From this S-S distance, the radius of S atom should be 1.65Å. This is about 60 % longer than that (1.03Å) estimated from the above Ni-S distance.

There are three Ni-S and six Ni-Ni “interlayer” bondings that hold the GB structure between GB0(GB1) and GB4 planes as shown in Table S1. After S atom segregate to the GB2 site as shown in Table S2, there are four Ni-S and three Ni-Ni interlayer bondings which are expected to hold the GB structure. However, the repulsive interaction of only
the two S(GB0)-S(GB2) pairs expand those Ni-Ni and Ni-S interlayer bondings.

We can not determine the fixed size of S atom in this case. For this reason, we think that we should not use the concept of atomic “size effect” to explain this GB expansion.

Table S1: The lengths of Ni-Ni and Ni-S bondings under 3.0 Å in the case of (GB0 4/4) segregation. The number in pharenthesis is the number of bondings. The lengths of interlayer bondings that hold the GB structure between GB0(GB1) and GB4 planes are underlined.

<table>
<thead>
<tr>
<th>GB0(S)</th>
<th>GB1(Ni)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GB-4(Ni)</td>
<td>2.87(1)</td>
</tr>
<tr>
<td>GB-3(Ni)</td>
<td>2.17(1) 2.76(2)</td>
</tr>
<tr>
<td>GB-2(Ni)</td>
<td>2.27(2) 2.65(2),2.69(1)</td>
</tr>
<tr>
<td>GB0(S)</td>
<td>2.25(1),2.44(2)</td>
</tr>
<tr>
<td>GB1(Ni)</td>
<td>2.25(1),2.44(2)</td>
</tr>
<tr>
<td>GB2(Ni)</td>
<td>2.27(2) 2.65(2),2.69(1)</td>
</tr>
<tr>
<td>GB3(Ni)</td>
<td>2.17(1) 2.76(2)</td>
</tr>
<tr>
<td>GB4(Ni)</td>
<td>2.87(1)</td>
</tr>
</tbody>
</table>

Table S2: The lengths of bondings after all Ni atoms at GB2 sites are replaced by S atoms. We can see that some bondings are expanded comparing with table S1.

<table>
<thead>
<tr>
<th>GB0(S)</th>
<th>GB1(Ni)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GB-4(Ni)</td>
<td>2.58(1)</td>
</tr>
<tr>
<td>GB-3(Ni)</td>
<td>2.26(1) 2.57(2)</td>
</tr>
<tr>
<td>GB-2(Ni)</td>
<td>2.25(2) 2.49(1),2.51(2)</td>
</tr>
<tr>
<td>GB0(S)</td>
<td>2.32(1),2.43(2)</td>
</tr>
<tr>
<td>GB1(Ni)</td>
<td>2.32(1),2.43(2)</td>
</tr>
<tr>
<td>GB2(S)</td>
<td>3.31(2) 3.31(2),4.18(1)</td>
</tr>
<tr>
<td>GB3(Ni)</td>
<td>2.45(1) 3.67(2)</td>
</tr>
<tr>
<td>GB4(Ni)</td>
<td>3.83(1)</td>
</tr>
</tbody>
</table>

(g) Eberhart’s speculation

From cluster calculations, Eberhart et al. (S10) have made the speculation that sulfur atoms began to attract each other in nickel GB at some concentration. In their cluster model, however, two sulfur atoms see each other across a triangular plane consisting of
only three nickel atoms. We think that this is far from the nickel-rich situation in which S-S repulsive interaction works as we stated in text. On the other hand, sulfur can form \( S_2 \) dimers in a sulfur-rich situation like that in \( \text{NiS}_2 \) ordered alloy. Considering those things, we think that the speculation by Eberhart et al. is at least valid for sulfur-rich situation.

(h) **Tensile test calculations from first-principles**

For strict tensile tests, we should include relaxations of atomic geometry and \( ab \) axes under the uniform strain along \( c \) axis. However, the atomic geometry optimization under stressed conditions are difficult to converge and very time-consuming in our experience. In addition, we confirmed that the overall magnitudes of the maximum tensile stress are in the same order with and without such relaxations. For these reasons, we show the results of simple tensile test as stated in text. This simple test is a convenient method to measure the tensile (cohesive) strength between the two specified fractured surfaces.

(i) **Definition of the GB expansion**

To see the relation between the tensile strength and lattice expansion due to impurities, the length of GB expansion, \( l_{GB} \) (Å), is defined as follows.

\[
l_{GB} = (c_{GB} - c_{bulk}) - \frac{1}{2}(c_{cleanGB} - c_{bulk})
\]

Here, \( c_{GB} \), \( c_{cleanGB} \), and \( c_{bulk} \) indicate the \( c \)-axis length of the GB unit cell including impurities, clean GB unit cell, and bulk unit cell, respectively. There are two GB planes in the GB unit cell, one of which includes impurity atoms and the other does not. For this reason, the second term that is the GB expansion of clean GB unit cell is extracted from the first term.
(j) Ideal shear strength

From Mackenzie’s method ($S11$), the ideal shear strengths of Aluminum (Al) and Copper (Cu) are estimated to be 0.9~2.62 and 1.2~1.29 GPa, respectively. With a precise method to determine the strength from first-principles calculations, however, Ogata et al. ($S12$) have recently shown that the ideal (pure) shear strengths of Al and Cu are 2.84 and 2.16 GPa, respectively. The ideal shear strength of nickel should also be determined from such a precise first-principles calculation.

(k) Calculations for phosphorous and boron

We performed similar calculations for phosphorous and boron instead of sulfur. The calculated segregation energies are summarized in Table S3, and the stress-displacement curves are plotted in Fig. S2 and S3.

The segregation energy of phosphorous (P) at GB0 site is 1.26 eV/P, which is a little small but close to that of sulfur, 1.73 (eV/S) in Table 1 in the main text. Similarly, the segregation energy of P at GB2 site is 1.24 eV/P. The energy loss from the repulsion between P atoms at neighboring GB0 and GB2 sites is very large. For example, supposing that P occupies gradually at GB2 sites in addition to all GB0 sites, the average segregation energy reduces from 1.45 eV/P (GB0 4/4) to 0.08 eV/P (GB0 4/4, GB2 4/4). As can be seen occupation curves in Fig. 2A in the main text, P can not fully occupy at GB0 and GB2 sites in the conditions (temperature and concentration) presented in the figure. In such a situation, a dense segregation that may cause a strong GB decohesion is difficult to occur. The stress-displacement curves for P case are plotted in Fig. S2. It is interesting that the tensile strength increases when the GB0 sites are fully occupied by P and then decreases with the addition of P at GB2 sites. Even when GB0 and GB2 sites are supposed to be fully occupied by P, the calculated tensile strength is still 10 GPa, which is much
larger than sulfur case (2.5GPa) in the main text. From these results, we can say that P does not have a strong embrittling effect like S for \( \Sigma 5(012) \) GB. Although this result is obtained only for \( \Sigma 5(012) \) GB case, this is consistent with the experimental fact that the embrittling potency of P is only 1/15 of S estimated by Bruemmer et al. (S13)

The segregation energies for B cases are also shown in Table S3 and the stress-displacement curves in Fig. S3. From Fig. S3, we can see that any segregation does not reduce the tensile strength and even enhance. From these results, we can understand that boron is a cohesion enhancer for Ni\( \Sigma 5(012) \) GB.

<table>
<thead>
<tr>
<th>P</th>
<th>site and occ.</th>
<th>(-\Delta \Delta E_{\text{seg}}(\text{eV/atom}))</th>
<th>site and occ.</th>
<th>(-\Delta \Delta E_{\text{seg}}(\text{eV/atom}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>GB0 1/4</td>
<td>1.26</td>
<td>GB1 1/4</td>
<td>-0.22</td>
<td></td>
</tr>
<tr>
<td>GB2 1/4</td>
<td>1.24</td>
<td>GB3 1/4</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>GB4 1/4</td>
<td>0.23</td>
<td>GB5 1/4</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>GB6 1/4</td>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GB0 4/4</td>
<td>1.45</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GB0 4/4, GB2 1/4</td>
<td>0.92</td>
<td>GB0 4/4, GB2 2/4</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>GB0 4/4, GB2 3/4</td>
<td>0.28</td>
<td>GB0 4/4, GB2 4/4</td>
<td>0.08</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>B</th>
<th>site and occ.</th>
<th>(-\Delta \Delta E_{\text{seg}}(\text{eV/atom}))</th>
<th>site and occ.</th>
<th>(-\Delta \Delta E_{\text{seg}}(\text{eV/atom}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>GB0 1/4</td>
<td>1.41</td>
<td>GB1 1/4</td>
<td>-0.74</td>
<td></td>
</tr>
<tr>
<td>GB1i* 1/4</td>
<td>0.88</td>
<td>GB2 1/4</td>
<td>1.24</td>
<td></td>
</tr>
<tr>
<td>GB3 1/4</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GB0 4/4</td>
<td>1.45</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GB0 4/4, GB1i 1/4</td>
<td>1.24</td>
<td>GB0 4/4, GB1i 2/4</td>
<td>1.08</td>
<td></td>
</tr>
<tr>
<td>GB0 4/4, GB2 1/4</td>
<td>1.13</td>
<td>GB0 4/4, GB2 2/4</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>GB0 4/4, GB2 3/4</td>
<td>0.69</td>
<td>GB0 4/4, GB2 3/4</td>
<td>0.54</td>
<td></td>
</tr>
</tbody>
</table>

*The GB1i site is an interstitial site that is located on the GB1 plane.
References and notes


**Figure legend**

**Figure S1**
Calculated density of states. (A) Total DOS and partial DOS of Ni at GB1 site for clean GB case. (B) Total DOS and partial DOS of S at GB0 site when GB0 sites are fully occupied by sulfur. We can see that sulfur hybridizes well with nickel. (C),(D) Total DOS and partial DOS of S at GB0 site and GB2 site, respectively, when GB0 and GB2 sites are fully occupied by sulfur. (E),(F) Total DOS and partial DOS of S for alpha-S and NiS$_2$, respectively. DOS of sulfur in C and D cases resembles that in B case. This indicates that the hybridization between sulfur atoms at GB0 and GB2 sites is weak. However, the energy levels for sulfur in C and D cases are slightly higher than that of B. This probably indicates the total energy increase by the repulsion between sulfur atoms. From E and F, we can see that the energy bands of S-S bonding are formed in a wide range from $-7 \sim -8$eV to Fermi level (0eV). This is contrast to the fact that Ni-S bondings are mainly formed from $-7 \sim -8$eV to $-5$eV as shown in B, C, and D. This indicates that Ni-S bonding is more stable than S-S bonding.

**Figure S2**
Stress-displacement curves calculated from first-principles for a Ni-P system.

**Figure S3**
Same as Fig. S2 for a Ni-B system.
Figure S1: M. Yamaguchi et al.
Figure S2: M. Yamaguchi et al. (Ni-P system)
Figure S3: M. Yamaguchi et al. (Ni-B system)