The effects of Vanadium on the strength of a bcc Fe $\Sigma 3(111)[1\bar{1}0]$ grain boundary

Sungho Kim$^1$, Seong-Gon Kim$^2$, Mark F. Horstemeyer$^1$, Hongjoo Rhee$^1$

$^1$Center for Advanced Vehicular Systems, Mississippi State University, P. O. Box 5405, Mississippi State, MS 39762, USA
$^2$Department of Physics and Astronomy, Mississippi State University, Mississippi State, MS 39762, USA

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Abstract

The effects of micro-alloying element, vanadium, on a bcc Fe $\Sigma 3(111)[1\bar{1}0]$ symmetric tilt grain boundary strength are studied using density functional theory calculations. The lowest energy configuration of the grain boundary structure are obtained from the first-principles calculations. The substitutional and interstitial point defect formation energies of vanadium in the grain boundary are compared. The substitutional defect is preferred to interstitial one. The segregation energies of vanadium onto the grain boundary and its fractured surfaces are computed. The cohesive energy calculation of the grain boundary with and without vanadium show that vanadium strengthen the bcc iron $\Sigma 3(111)[1\bar{1}0]$ grain boundary.

Introduction

The macroscopic behavior of steel alloy and their capabilities for technological applications are vitally influenced by the properties of micro-alloying elements in their microstructures. Small amounts of microalloying elements such as vanadium (V), titanium (Ti), or niobium (Nb) increase strength of steels by grain size control, precipitation hardening, and/or solid solution hardening\[2,1\]. V, Nb, and Ti combine preferentially with carbon and/or nitrogen to form a fine dispersion of precipitated particles in the steel matrix. Nb may be added in high strength low alloy (HSLA) sheet to increase the strength predominately via grain refinement, while other microalloys apply the strengthening mechanism of precipitation hardening to a major extent(Ti) or totally(V)\[14,15\]. The addition of small amounts of V increases the yield strength and the tensile strength of carbon steel. V is one of the primary contributors to precipitation strengthening in microalloyed steels. When thermomechanical processing is properly controlled, the ferrite grain size is refined and there is a corresponding increase in toughness. V also increases hardness, creep resistance, and impact resistance due to formation of hard vanadium carbides limiting grain size. Since V is very effective on aforementioned properties, it is added in minute amounts. At greater than 0.05%, however, there may be a tendency for the steel to become embrittled during thermal stress relief treatments\[6,13\].

The cohesion at these grain boundaries affects the hardness, deformability, and toughness of the material and it can be enhanced or decreased by segregated impurities. Therefore, it is essential to understand the interfacial cohesion and impurity segregation in detail, and a meaningful goal is to find general rules that describe the relationship between these microscopic features and the macroscopic properties.

The vanadium(V) is the most common cohesion enhancer that changes the strength of iron(Fe) metal by the segregation at grain boundaries. The grain boundary segregation occurs within a few atomic layers at the grain boundary plane. The grain boundary cohesion enhancement is caused by the change in the cohesive properties of atoms within a few atomic layers at the grain boundary plane.

In 1989, Rice and Wang\[12\] developed their theoretical model for solute segregation into grain boundary and insisted that the energy required for interfacial separation of grain boundary is the most important contribution to embrittlement of the grain boundary. They used the solutes (C, P, S, Sb, Sn) in iron to show that the segregation-induced change of separation energy of grain boundary is roughly consistent with segregation-induced embrittlement. They estimated the separation energy from experimental segregation energies in fractured surface and grain boundary.

A fracture of the grain boundary creates two separate fractured surfaces under the action of stress. The cohesive energy of grain boundary $\gamma_{coh}$ (J/m$^2$) is defined as the energy difference between the en-
ergy sum of two surfaces after fracture and the grain boundary energy before fracture.

\[ \gamma_{coh} = 2\gamma_s - \gamma_{gb} \] (1)

where \( \gamma_s \) is the surface energy of the two fracture surfaces after fracture, and \( \gamma_{gb} \) is the grain boundary energy before fracture. The cohesive energy in the presence of segregations of solute atoms can be defined as follows:

\[ \gamma_{coh}^{seg} = (2\gamma_s - \frac{N E_{seg}^s}{A}) - (\gamma_{gb} - \frac{N E_{seg}^{gb}}{A}) \]

\[ = \gamma_{coh} - (E_{seg}^s - E_{seg}^{gb}) \frac{N}{A} \] (2)

where \( E_{seg}^s \) and \( E_{seg}^{gb} \) are the segregation energy on the surface and grain boundary. The \( N \) is the number of atoms in the unitcell. The \( A \) is the area of surface or grain boundary.

The grain boundary segregation and trapping of vanadium atoms at the fracture surface affect the cohesive energy of the grain boundary[10, 26, 4, 19, 8, 3, 22, 3, 28, 27, 13, 25, 21, 26, 17, 23]. If the fracture surface segregation energy is larger than the grain boundary segregation energy for a solute element, this element can reduce the cohesive energy of the grain boundary; it indicates that this element is an embrittling element. If the grain boundary segregation energy is larger than the fracture surface segregation energy for a solute element, on the other hand, this element is a strengthening element. We assume that the total amount of segregated solute atoms does not change during fracture. This assumption is valid for elements like vanadium. Fig. 1 shows the schematic of the cohesion enhancement effect on a grain boundary by solute atom segregation at the grain boundary.

**Computational Methods**

All computation in this paper employed the electronic structure calculations based on the first principles density-functional theory (DFT)\[7, 24\] using the projector-augmented-wave method.\[5, 16\] All calculations were spin polarized and the Voskown analysis is used for the magnetic moment calculations. The wave function of electrons are expanded in terms of plane-wave basis set and all plane waves that have kinetic energy less than 250 eV are included in expanding the wave functions. For the treatment of electron exchange and correlation, we use the generalized gradient approximation (GGA) using Perdew-Burke-Ernzerhof scheme.\[11\] For the determination of the self-consistent electron density 4×1×3 Monkhorst-Pack k-point set has been used. The structure optimizations were performed until the energy difference between successive steps becomes less than 10⁻³ eV.

Fig. 2 shows simulation box and atom configuration. Two layers are in the periodic cell in \([1\bar{1}2]\) direction. The grey balls represent iron atoms. Four layers are periodic in \([1\bar{1}0]\) direction. The Fe bcc \(\Sigma 3(111)[1\bar{1}0] \) grain boundary is indicated with a black arrow. The total number of atoms in the simulation box is 88. The periodic boundary conditions are used in all three direction. Spin is not considered.

**Vanadium interaction with the grain boundary and the fractured surface**

We obtained the optimized grain boundary structure of Fe bcc \(\Sigma 3(111)[1\bar{1}0] \) shown in Fig. 2. The atoms in first neighbor layers near the grain boundary are relaxed from regular bcc site most significantly. The other atoms doesn’t change their posi-
The optimized grain boundary structure of Fe BCC $\Sigma 3(111)[\bar{1}\bar{1}0]$, and simulation box and configuration. There are no vacuum and periodic conditions apply in three directions. Two layers are periodic in $[\bar{1}12]$ direction. The grain boundary is indicated by a black arrow. The atoms in first neighbor layers near the grain boundary are relaxed from regular bcc site most significantly.

The grain boundary formation energy per unit area is 0.113 eV/Å$^2$ which is the energy required the grain boundary to form from the Fe bcc bulk.

The grain boundaries usually have many hollow sites bigger than normal between atoms. The hollow sites are good candidate for micro-alloying element segregation. In our unitcell there are two hollow sites. We calculated the vanadium interstitial formation energy in one hollow site out of two. A vanadium atom is placed at a few different places in a hollow site to find the best vanadium site to lower the system energy. Fig. 3 show the best interstitially vanadium-segregated grain boundary structure. The vanadium atom is in the plane of front layer and shifted a little bit in $[1\bar{1}0]$ direction. The vanadium push away a little bit the upper and lower neighbor iron atoms because the two iron atoms are too close to the vanadium atom.

The vanadium interstitial formation energy on the grain boundary is -4.20 eV from a isolated vanadium atom and -0.75 eV from a vanadium atom in bulk. The negative sign means that the vanadium substitution for iron atom on grain boundary is an exothermic process. Compared to interstitial formation energy, the substitutional formation energy is lower by 1.8 eV which means that substitution defects occur far more often than interstitial defects in real world. Therefore we only consider the substitutional segregation at the grain boundary.

The vanadium substitutional formation energy on the grain boundary is -6.08 eV from a isolated vanadium atom and -0.75 eV from a vanadium atom in bulk. The vanadium substitutional formation energy into the grain boundary is the difference of the grain boundary formation energy from vanadium defect formation energy in bulk. In order to calculate the vanadium segregation energy into the grain boundary we calculated two vanadium point defect formation energies in bulk. One is interstitial point defect formation energies which are -1.36 eV for tetrahedral interstitial from isolated vanadium atom and 3.97 from bulk vanadium atom while octahedral interstitial defect energies are higher by 0.43 eV. The other is substitu-
Figure 4: The optimized structure of substitutionally segregated vanadium atom on Fe bcc Σ3(111)[110] grain boundary. The grey balls represent iron atoms and white vanadium.

tional point defect formation energy which is -6.06 eV from isolated atom and -0.73 eV from bulk atom. The substitutional defect formation energies in bulk are again lower than interstitial one by 4.70 eV. From the calculated energies we can conclude that vanadium atoms exist mostly as substitutional defects in bulk and segregate into substitutional defects in grain boundary.

The effect of vanadium on the grain boundary

The vanadium segregation energy from bulk to grain boundary is the substitutional defect formation energy in bulk substracted by the substitutional defect formation energy in bulk. We calculated the segregation energy which is -0.03 eV. The negative sign mean that the segregation is an exothermic process.

The surface formation energy of (111) is calculated and 0.167 eV/Å² per unit area. The vanadium segregation energy from bulk into surface is calculated to be -9.57 eV. The negative represent that segregation is an exothermic process.

The grain boundary cohesion energy(GBCE) defined in Eq. 1 without vanadium is calculated as 1.43 eV. The GBCE with segregated vanadium is 1.54 eV. The vanadium segregation increases GBCE by 0.11 eV or 0.066 J/m².

According to our DFT calculation results we can conclude that the segregated vanadium atom in grain boundary strengthen the grain boundary against the brittle grain boundary fracture.

Summary and Conclusions

In summary, we studied the effects of Vanadium on a bcc iron Σ3(111)[110] grain boundary strength. We calculated the optimized grain boundary structure and the best vanadium segregation site on the grain boundary. We compared the interstitial defect formation energy to the substitutional one in bulk and the grain boundary. The substitutional formation energy is lower than interstitial segregation energy. Our results indicate that the substitutional segregation is more desirable. We also calculated vanadium segregation energies on the fractured surface of the grain boundary. Based on those segregation energies we calculated the cohesive energy of the grain boundary and vanadium segregation effect on cohesive energies.

In conclusion, vanadium atom mostly exist as substitutional defects rather than interstitial defects in both bulk and grain boundary. Our first-principle calculations show consistently with experiment that vanadium is a Fe grain boundary cohesion enhancer and strengthens the Fe bcc Σ3(111)[110] grain boundary.

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