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Effects of solute size on solid-solution hardening in vanadium alloys: A first-principles calculation

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We performed first-principles calculations to quantify the effect of 26 transition metals on the mechanical properties of vanadium (V) alloys. The generalized stacking-fault (GSF) energies of the solutes were evaluated in three slip systems. Solutes with similar atomic radii to that of V present high GSF energies, which increase the energy barrier for double-kink nucleation and result in excellent strengthening effect. This size effect indicates that noble metals can significantly improve the mechanical strength of V alloys.

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Vanadium (V) alloys are interesting potential materials for first-wall structures of fusion reactors because of their remarkable high-temperature mechanical properties in the fusion environment [1–5]. Recent studies on developing V alloys have focused on optimizing the alloy composition and microstructure by adding solute atoms in their design to improve their properties [2]. The presence of dislocation activity on two or more slip planes is a common phenomenon during plastic deformation in bcc materials [6,7]. Moreover, non-basal slip systems can be activated by adding solutes based on the predicted variation of stacking-fault energies [8,9]. Thus, determining the effects of solute atoms on the mechanical behavior of materials, on the alloy design, and on process design strategies is important for practical applications.

From a traditional point of view, the solute effect on alloys is caused by solid-solution hardening (SSH), which is closely related to the differences in atomic radii or elastic moduli between the solute and matrix atoms. Specifically, in considering solute atoms in a given host lattice, it is commonly believed that considerable differences among lattice parameters are assumed to result in a more significant SSH effect [10,11]. This hypothesis is based on the high local stress fields introduced by solute atoms. However, we obtained an unexpected trend in this study, in which solute atoms with large differences among lattice parameters are not always harder than those with low difference.

This work aimed to elucidate the origins of the solute effect of a set of V alloys. A series of first-principles calculations were performed to quantify the solute effect of 3d, 4d, and 5d transition metals on the mechanical properties of V alloys. The generalized stacking-fault (GSF) energies were determined in the (110)<111>, (112)<111>, and (123)<111> slip systems. The results are then calculated and discussed.

The calculations were performed using the Vienna Ab Initio Simulation Package (VASP) [12,13] via the projector augmented wave (PAW) method [14,15] and the Perdew–Burke–Ernzerhof function of generalized gradient approximation (GGA-PBE) [16]. A $3 \times 3 \times 3$ supercell was used to calculate the solution energies of solute atoms in V alloys. The energies are obtained with a 400 eV plane-wave cutoff and a $5 \times 5 \times 5$ Monkhorst–Pack mesh of k-points. These calculations are fully relaxed in terms of volume, shape, and atomic positions. The atoms are considered fully relaxed when the Hellmann–Feynman forces acting on them are lower than 0.02 eV/Å. The present equilibrium lattice constant for bulk V is 2.99 Å, which is consistent with theoretical results [17,18] and the experimental value of 3.03 Å [19].

To evaluate the solute effects, we constructed V supercells containing 54, 60, and 45 atoms with one doping atom for predicting GSF energies in the (110)<111>, (112)<111>, and (123)<111> slip systems, respectively. The Monkhorst–Pack mesh of k-points was selected to ensure a convergence result: $3 \times 3 \times 1$ for the (110)<111> and (112)<111>, and $3 \times 4 \times 1$ for the (123)<111> slip systems. A vacuum width of 10 Å was added to periodical slabs for all configurations. The SFE curves were generated with ten equally spaced rigid shifts of the two parts of the crystal. For each rigid shift, the atomic positions are relaxed along the Z-axis ([111] direction) by minimizing the forces to less

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than 0.02 eV/Å on each atom. The atoms at the top and bottom layer are fixed during relaxation.

Solution energy was calculated with the following equation to investigate the solubility of solute atoms in V [20]:

$$E_s = E_{tot} - nE_v - E_{sol} \qquad (1)$$

where E_{tot} is the total energy of the supercell containing one solute atom at the substitutional site, and E_v and E_{sol} are the energies of the pure crystal V and the solutes in their elemental ground-states, respectively. The GSF energy γ_{US} can be formally defined as [21,22]:

$$\gamma_{US} = \frac{1}{S}(E_{SF} - E_0) \qquad (2)$$

where E_{SF} and E_0 are the free energies of the supercell after and before shear deformation, respectively, and S is the area of the faulted region. The solute volume V_{sol} is also calculated using the following expression to determine the atomic size of each solute impurity [23]:

$$V_{sol} = V_{cont-sol} - V_{tot} \qquad (3)$$

where $V_{cont-sol}$ and V_{tot} are the volume of the supercell with and without a single solute atom, respectively.

We initially investigated the effect of solute size on the solution energy of V. Figure 1 presents the solution energies of the solute atoms at substitutional sites as a function of atomic number of 3d, 4d, and 5d transition elements, along with the atomic radius of solutes [24]. From a thermodynamic perspective, a negative solution energy indicates an exothermic process and a positive energy denotes an endothermic process [20]. As shown in Figure 1, it is evident that the solution energies initially decrease and then increase with increasing atomic number in the periodic table. The solution energies exhibit a similar trend to the increasing atomic sizes of solutes, which suggests that the solution energy is also strongly related to atomic size. In particular, the larger atomic sizes of solutes (such as Sc, Y, Zr, La, and Hf) are presented with higher positive solution energies, thereby indicating that the dissolution of large atoms in V is not energetically favorable. These conclusions are in good agreement with the Hume–Rothery rules, where the atomic diameters of the solute and solvent atoms must differ by no less than 15% to form a substitutional solid solution [25]. Recently, Hua et al. [26] showed that the solution energy of Ti atoms in the substitutional site of bulk V is 0.22 eV, which is lower than our result (0.308 eV). This discrepancy may be due to the different pseudo-potential functions and parameters used in the calculations.

To understand the influence of solutes on the mechanical properties of V alloys, it is important to investigate the GSF energy, which denotes the lowest energy barrier for dislocation nucleation [27] and is considered as an appropriate parameter to describe the solution effect rather than size and modulus mismatch [28]. Figure 2(a) demonstrates that the GSF energy of pure V in the $(1\bar{1}0)\langle111\rangle$ slip system is 617 mJ/m^2, which is consistent with the reported value [29] when the differences in calculation formulas are ignored. This value is also the lowest among the three systems, indicating that the dislocation activities of the (110) slip system possibly occur in bcc V and has a dominant function in plastic deformation. When considering the solute effect, the GSF energy values for 26 solute atoms added in the $(1\bar{1}0)\langle111\rangle$ slip systems are summarized in Figure 2(a) with the dependence of atomic radius. Evidently, the rough distribution point of GSF energies for the added solutes demonstrates a distinct dependency on the atomic sizes. This size effect can be described as follows: the larger the differences in atomic radii between solutes and V, the lower the GSF energy values (such as Sc, Y, Zr, and La). This phenomenon is in agreement with the investigation by Wang et al. [30] on the effect of doping atoms on the GSF energies of Mg alloys. Moreover, the GSF energy values increase significantly after adding noble metals, such as Ru, Rh, Os, Re, and Pt. In particular, the increase is up to 18% after Ir addition, thereby indicating that noble metals can significantly improve the mechanical properties of V alloys because of their similar atomic size to that of V. By contrast, large-size solutes exhibit low GSF energy, thereby promoting the formation of stacking faults from the large lattice distortion and activating the slip systems to improve ductility during plastic deformation. In the case of the Y solute with large differences in the atomic radii to matrix Mg atom, Sandlöbes et al. [31] demonstrated that ductility increases when adding Y solutes to Mg in Mg–Y alloys.

The effect of solutes on the GSF energies in the $(1\bar{1}2)\langle111\rangle$ and $(1\bar{2}3)\langle111\rangle$ slip systems were also investigated. Figure 2(b) and (c) shows that the size effect of these solutes remains similar to those in the $(1\bar{1}0)\langle111\rangle$ slip system; in addition, the GSF energies in the $(1\bar{2}3)\langle111\rangle$ system effectively increase than those in the $(1\bar{1}2)\langle111\rangle$ system. Other observational studies also provided useful information. For example, the GSF energy increases in the $(1\bar{1}0)\langle111\rangle$ systems by adding Cu but decreases in the $(1\bar{1}2)\langle111\rangle$ and $(1\bar{2}3)\langle111\rangle$ slip systems. This result suggests that Cu solutes can help improve the activation of their corresponding slip systems because of their reduced GSF energies.

The average GSF energy factor can be constructed to balance the roles of each system during plastic deformation in assessing the solute effect and in evaluating the effects of alloying elements on deformation ability [30]. The detailed expression can be written as [30]:

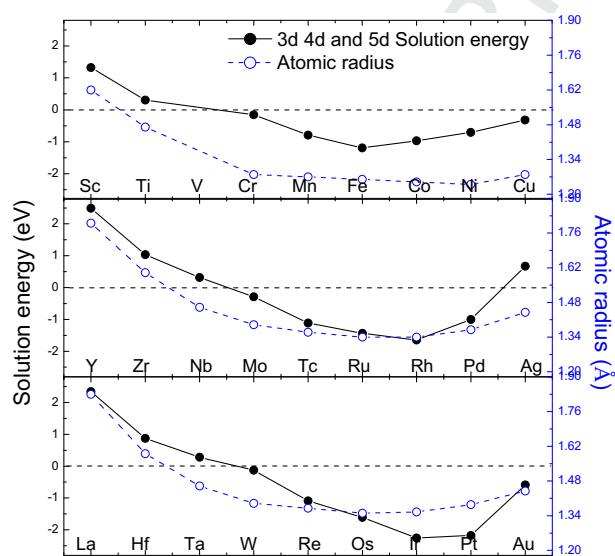$$E = \sum_{i=1}^{3} \frac{(\gamma_{us}^i)^2}{\sum \gamma_{us}^i} \qquad (4)$$

Figure 1. Solution energies of 3d, 4d and 5d solute atoms as a function of atomic number in V.