Preferential diffusion in concentrated solid solution alloys: NiFe, NiCo and NiCoCr

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Abstract

Single-phase concentrated solid solution alloys, including high entropy alloys, exhibit remarkable mechanical properties as well as extraordinary corrosion and radiation resistance compared to pure metals and dilute alloys. However, the mechanisms responsible for these properties are unknown in many cases. In this work, we employ *ab initio* molecular dynamics based on density functional theory to study the diffusion of interstitial atoms in Ni and Ni-based face-centered cubic concentrated alloys including NiFe, NiCo and NiCoCr. We model the defect trajectories over 100 ps and estimate the tracer diffusion coefficients, correlation factors and activation energies. We find that the diffusion mass transport in concentrated alloys is not only slower than that in pure components, i.e. sluggish diffusion, but also chemically non-homogeneous. The results obtained here can be used to understand and predict atomic segregation and phase separation in concentrated solid solution alloys under irradiation.

1. Introduction

Single-phase concentrated solid solution alloys (SP-CSAs), including high entropy alloys (HEAs), have attracted great interest in the material science community recently [1]. In contrast to traditional alloys, CSAs are comprised of two or more principal elements in near or equal concentrations [2]. Many exceptional properties of SP-CSAs have been observed experimentally, such as high-temperature stability and hardness [3], excellent corrosion and wear resistance, and improved fatigue and fracture resistance [4,5]. In particular, it was demonstrated that Ni-based face-centered cubic (*fcc*) SP-CSAs exhibit great potential for applications in the nuclear industry because of their superior radiation resistance [6–9]. The suppression of damage accumulation was revealed with increasing complexity from pure nickel to more complex CSAs [10,11]. However, the mechanism behind the observed radiation resistance is still elusive.

Diffusion of lattice defects is the main mechanism responsible for the structural evolution of materials under different conditions including radiation and thermal treatment. During irradiation, energetic particles produce a large number of vacancies and interstitials and their evolution is the key in understanding radiation effects. In pure metals, interstitials are highly mobile compared to vacancies. In SP-CSAs, the random arrangement of multiple species creates extreme chemical disorders, leading to significant local lattice distortions and atomic displacements that affect defect formation and migration energies, thus contributing to defect formation and evolution [6,10,12]. This effect is stronger for interstitials due to the accompanied larger structural perturbations. As it was shown in [11] using the climbing image nudged elastic band (CI-NEB) method, the migration barriers of interstitials and vacancies are widely spread due to the local chemical disorder inherent in SP-CSAs. Moreover, each particular defect jump

has its own migration barrier, pre-exponential and correlation factors, and therefore the estimation of effective diffusion properties is not obvious. Another issue ignored in static calculations is the temperature effect, which is important for defect evolution since diffusion activation energies and related pathways are strongly dependent on thermal lattice vibrations. A detailed knowledge of the temperature activated defect diffusion in SP-CSAs is essential for understanding and predicting the microstructural evolution under irradiation.

The above limitations can be resolved by molecular dynamics (MD) which simulates atomic vibrations directly thus allowing the migrating atom to find the optimal diffusion pathway according to the potential energy landscape. If the simulated trajectory is long enough to ensure statistics of different jumps, and interatomic interactions are accurately described, classical MD (CMD) is capable of modeling the diffusion process with a high accuracy. However, there are no reliable interatomic potentials able to account for the main features of multicomponent concentrated alloys even qualitatively [12]. Currently, density functional theory (DFT) is the only technique that can accurately consider chemical effects in such complicated materials and DFT based *ab initio* MD (AIMD) is an important tool in studying diffusion problems with unprecedented accuracy and predictive capability. Due to high computational cost, AIMD is limited by a small supercell size and relatively short simulation time. However, it can produce unique knowledge of defect behaviors where local chemical effects are important. In this regard, AIMD has been successfully used to study He interstitial diffusion in α -Fe [13], self-interstitial atom diffusion in Si [14] and some ferritic dilute alloys[15], and H diffusion in liquid Al [16].

In this work, we apply AIMD to study interstitial atom diffusion in pure Ni and its *fcc* equiatomic random NiFe, NiCo and NiCoCr alloys. The results for NiFe are compared to those from CMD using available embedded atom method (EAM) potentials. The present study

provides detailed information on tracer diffusion coefficients, diffusion mechanisms, activation energies and correlation factors for the diffusion of a single interstitial atom in these CSAs. In addition, we have investigated the accuracy of MD modeling with a limited trajectory length regarding the calculation of diffusion coefficients. Our results reveal a preferential diffusion mechanism in CSAs depending on the structural and chemical details of the alloys.

2. Computational methods

All AIMD simulations were performed using the DFT-based Vienna *Ab Initio* Simulations Package (VASP) [17]. The generalized gradient approximation with the Perdew-Burke-Ernzerhof form [18] was used to describe the exchange-correlation functional, and ion-electron interactions were modelled by projector-augmented wave method [19]. A cubic $3\times 3\times 3$ supercell containing 108 atoms was employed. Only the Γ point was included in the dynamic simulations and an energy cutoff of 300 eV was used. The chemical disorder of CSAs was considered using the special quasirandom structure constructed by optimization of Warren-Cowley short range order parameters up to the fourth neighbor shell.[20,21] The structure of the initial solid solution was first optimized at different volumes by conjugate gradient method with an energy and force criterion of 10^{-4} eV and 10^{-2} eV/Å, respectively. The lattice constant was then obtained by fitting the calculated energy-volume curve to the Murnaghan equation of state [22] and the supercell volume was fixed in the following MD simulations. All calculations were spin polarized with the magnetic moments initialized by the data obtained from static calculations [12]. Specifically, Ni, Fe and Co are ferromagnetic whereas Cr is antiferromagnetic. A single [100] interstitial dumbbell was introduced randomly at one of the lattice sites to initiate the simulations. The

canonical NVT ensemble was employed and the temperature was controlled by the Nosé-Hoover thermostat [23,24] with a mass parameter of 1 a.m.u. Temperatures from 800 to 1400 K and from 1200 to 1800 K were considered for pure Ni and the CSAs, respectively. At each temperature, the defect structure was first equilibrated over 3 ps with a timestep $t_S = 1$ fs and then the diffusion data was collected from the subsequent >100 ps simulations with $t_S = 2$ fs. To calculate tracer diffusion coefficients, mean square displacement (MSD) of atoms was averaged over three independent AIMD simulations with different initial interstitial positions.

CMD simulations of interstitial atom diffusion were performed by the atomic/molecular simulator (LAMMPS) [25] using NVT ensemble with the Nosé-Hoover thermostat. The same temperatures as in AIMD were adopted. Three EAM potentials developed by Bonny *et al* [26–28] were used and a $8 \times 8 \times 8$ *fcc* supercell was employed. The simulation time was over 3 ns with $t_S = 2$ -5 fs depending on the temperatures.

Atomic trajectories were obtained in MD directly from atomic positions known at each time step. The defect trajectory was recorded as a sequence of defect position after each jump. To detect the instant defect position, the Wigner-Seitz cell analysis (see Appendix A) was used. Atomic and defect trajectories were used to estimate the corresponding diffusion coefficients, activation energies and correlation factors as described in Appendix A. Appendices B and C describe accuracy analysis of diffusion modeling in the limited time affordable for AIMD.

3. Results

3.1 Pure Ni

The atomic MSD calculated by averaging over different time origins as described in Appendix A shows practically a linear function of time, describing a diffusion process. The

tracer diffusion coefficients calculated by Eq.A1 are presented as a function of the reciprocal temperature in Fig.1 together with those calculated using three sets of EAM potentials [26–28]. The error bars in the simulation results represent the standard deviation of the mean calculated from three independent simulations at each temperature. An Arrhenius fit to these data yields the activation energies (E_a) and pre-exponential factors (D_0) as presented in the Table 1. Both E_a and D_0 obtained here are in good agreement with the earlier data by Barnard *et al* [15]: 0.13 eV and 4.31×10^{-8} m²/s vs 0.14 eV and 3.95×10^{-8} m²/s, respectively. It can be seen also that the Bonny2009 potential gives the same E_a as AIMD, whereas Bonny2011 and Bonny2013 potentials both overestimate E_a . In all the cases the effective activation energy due to interstitial atom diffusion in pure Ni is very close to the migration barrier of a [100] dumbbell calculated by CI-NEB at 0K, which is 0.13 eV, 0.33 eV, and 0.17 eV based on Bonny2009, Bonny2011 and Bonny2013 potential, respectively. Note that *ab initio* NEB calculation gave a value of 0.11 eV for single interstitial diffusion in Ni [12], consistent with E_a obtained from AIMD.

3.2 NiFe

Temperature dependent tracer diffusion coefficients due to interstitial atom diffusion in NiFe alloy obtained by AIMD and CMD using EAM potentials [26–28] are presented in Fig.2a. The activation energies and prefactors for total tracer diffusion and partial diffusion are summarized in Table 2. It can be seen that the effective activation energy of Ni diffusion in NiFe, E_a^{Ni} , is significantly larger than that in pure Ni. E_a^{Fe} for Fe diffusion in NiFe is also higher than the energy barrier in the dilute region, which is 0.11 eV calculated by the NEB method [27]. These activation energies fall into the range of migration energy distributions of Ni and Fe interstitials in NiFe calculated by *ab initio* NEB calculations [12]. Diffusivities of interstitials in

the NiFe alloy in all cases (i.e. AIMD and CMD with EAM potentials) are continuously lower than those in pure Ni which is evidence that modeling confirms a sluggish diffusion in CSAs. The main result found by AIMD is **the chemically-biased diffusion**: diffusion of interstitial atoms in an NiFe alloy produces displacements of Ni atoms about two times faster than Fe atoms, as shown in Fig. 2b for the ratio of partial diffusion coefficients D_{Ni}^* / D_{Fe}^* .

The diffusivities obtained by CMD using EAM potentials demonstrate different values as shown in Fig.2b. Bonny2009 potential predicts a lower diffusivity for Ni interstitials than Fe whereas an opposite trend is seen for both Bonny2011 and Bonny2013 potentials. In particular, Bonny2011 predicts a similar diffusivity as *ab initio* calculations. The activation energy from Bonny2011 is 0.32 eV, which is close to *ab initio* value of 0.36 eV. For Fe diffusion, AIMD gives a higher diffusivity as compared to CMD calculations and the activation energy is smaller than that obtained from all three empirical potentials. In this case, the diffusivity from Bonny2009 is the closest to the results of AIMD. As for the D_{Ni}^* / D_{Fe}^* ratio, Bonny2013 is the closest to the result from AIMD simulations, whereas Bonny2011 predicts a much higher **chemically-biased diffusion**: up to 10 at low temperature.

In the simulations, the interstitials are eventually in the form of [100]-type dumbbells where two atoms oriented along one of the [100] directions share the same lattice site. We have analyzed the nature of dumbbell atoms that form Ni-Ni, Ni-Fe and Fe-Fe pairs. The fraction of total time each dumbbell spent in a specific configuration at each temperature is presented in Fig.3 and a detailed distribution of the spent time in each configuration gathered by AIMD at 1400K is shown in Fig.4. It can be seen that the interstitials spend far more time in the form of Ni-Ni and Ni-Fe dumbbells than in the form of Fe-Fe dumbbells. This result is consistent with **the chemically-biased diffusion** described above as well as *ab initio* results about interstitial

formation energies in NiFe at 0K [12], where Fe-Fe dumbbells were reported to exhibit the largest formation energies while Ni-Ni dumbbells the lowest. All these results indicate unambiguously that interstitial atoms in NiFe alloys diffuse mainly via a Ni subsystem. As a consequence, the separation of Ni and Fe atom flow is a specific feature of the diffusion in NiFe under irradiation conditions where interstitial atoms are produced.

3.3 NiCo

Full and partial tracer diffusion coefficients determined by AIMD in the NiCo alloy are presented in Fig.5a. An Arrhenius treatment yields an activation energy of 0.36, 0.45 and 0.30 eV for the total, Ni and Co partial diffusion, respectively. The values of E_a and D_0 parameters given in Table 3 also demonstrate **a chemically-biased diffusion** as Co diffuses faster than Ni: $D_{Ni}^* / D_{Co}^* < 1$ as can be seen in Fig.5b.

The total time fractions of Ni-Ni, Ni-Co and Co-Co dumbbells are presented in Fig.6. It demonstrates that mixed Ni-Co pairs are the most frequent dumbbell configurations whereas Ni-Ni dumbbells are the least frequent. These results are fully consistent with earlier DFT results at 0K, which demonstrated that Ni-Co dumbbells exhibit the lowest formation energy while Ni-Ni dumbbells the highest [12]. The dominant configurations are therefore Co-containing dumbbells, contributing to preferential Co atoms diffusion as displayed in Fig.5.

3.4 NiCoCr

Full and partial tracer diffusion coefficients of interstitials in NiCoCr calculated by AIMD are presented in Fig.7a. The results of Arrhenius treatments (E_a and D_0) for these diffusion coefficients are listed in Table 4. For comparison, the ratios of partial diffusion coefficients are

provided in Fig.7b. All these results demonstrate that the diffusivity of Co and Cr **via interstitial** is larger than that of Ni. Accordingly, E_a of Co and Cr are close to each other (0.26 and 0.35 eV) and both are much lower than that obtained for Ni (0.60 eV).

The time fraction for each dumbbell type is given in Fig.8. The interstitials spent the most time in the Co-Cr form and the least time as Ni-Ni dumbbells. This is consistent with the result that the diffusion of Co and Cr is faster than Ni as obtained from tracer diffusion coefficient calculations (see Fig.7a). Note that in general the statistical properties of all partial diffusion coefficients are weaker in the three-component alloy than those in the two-component ones and this can be seen from the large error bars in Figs.7a and 8.

The correlation factor f_c calculated from angles between successive interstitial jumps (see Appendix A for details) in pure Ni, NiFe, NiCo and NiCoCr is shown in Fig.9 as a function of temperature. Note that f_c equals to 1 for totally uncorrelated jumps where all jumps to neighbouring sites are equally probable and independent of the prior jump, i.e. random walk. In practical modeling, f_c is always <1 because of the ‘dynamic memory’ of modelled crystal. In pure Ni the correlation factor slightly decreases from ~ 0.5 at low temperature to ~ 0.4 at high temperature, whereas in all studied alloys it increases from ~ 0.2 to >0.4 over the studied temperature range. Similar behaviors were also observed in CMD simulations for NiFe [29]. The low value of f_c in alloys contributes to the decreased tracer diffusion coefficients and thus to the sluggish diffusion in concentrated alloys. This is consistent with the tracer diffusion coefficients in alloys discussed above and in [30]. This effect is stronger at lower temperatures implying that the nature of this dynamic effect, at least partly, lies in different barriers for different defect jumps. In each alloy there are preferential migration pathways that limit the number of effective jump directions, since the probability of a particular jump depends on the

local environment in alloys. The probability of defect jumps within these preferential pathways should decrease when the fraction of the related alloying component decreases.

4. Discussion

The phenomenon of slow (sluggish) diffusion observed here in concentrated alloys can be explained by the difference in formation and migration energies of interstitial atoms in different CSAs. It was found that the formation energies of dumbbell defects in alloys such as NiFe and NiCo can be well below 4.0 eV depending on local configurations [12], which is lower than those in pure Ni, 4.27 eV. This leads to strong binding interactions between interstitial and lattice atoms within certain environments. Also, most migration barriers in concentrated alloys were shown to be higher than those in pure Ni [12]. This leads to sluggish diffusion in CSAs due to increased effective migration energies (because of high energy barriers) and decreased effective jump correlation factors (via reducing number of possible jumps below the coordination number of the lattice structure within the limited volume of low energy regions).

The slow diffusion of interstitial atoms in CSAs suggests that all processes where interstitial atoms participate should be delayed in time [31]. Because of the high formation energy of interstitial defects, they are formed mainly under irradiation with energetic particles such as ions or neutrons. There are direct and non-direct effects of defect diffusivity to the microstructure evolution in these alloys. Direct effects of sluggish interstitial diffusion include slower development of both void swelling (that occurs due to preferential absorption of interstitial atoms at dislocations, i.e. conventional bias) and interstitial clusters/dislocation loops population (that are created directly in high-energy displacement cascades and by interstitial

atoms clustering). The observed preferential interstitial configurations in each alloy lead to a strong non-direct effect related to the interstitial cluster mobility. Specifically, a single interstitial atom has the chance to adopt a preferential configuration, e.g. Ni-Ni pair in the Ni-Fe alloy. However, even a small cluster of interstitials formed in a concentrated alloy should include a number of energetically non-favorable atom pairs. This leads to an increase in the effective energy for the clusters migration which in turn reduces or even prevents cluster mobility. Therefore, the contribution from production bias, which is a very powerful swelling mechanism in pure metals and dilute alloys [30] can be significantly suppressed. It should be noted that the diffusion of vacancies in equiatomic binary CSAs is less affected compared to that in pure Ni, as indicated from the DFT calculated migration barriers [12] and direct CMD simulations [32]. Therefore, the sluggish diffusion of interstitials is likely to enhance the recombination between interstitials and vacancies and thus make the alloy more irradiation-resistant **in general**. [9] These expected effects are in line with experimental observations [6,8] that showed reduced swelling under ion irradiations.

Another important finding is **the chemically-biased diffusion** of interstitials. The highest partial diffusion coefficients in NiFe, NiCo and NiCoCr are presented in Fig.10. The diffusion of Ni in NiFe is preferential while the diffusion of Co dominates in NiCo and NiCoCr. These observations correlate with the low formation energies for Ni-Ni dumbbells in NiFe and Co-Co dumbbells in NiCo. The diffusion of Co and Cr dominates in NiCoCr, indicating the preference of Co-Cr dumbbells. Therefore, the trend of dumbbell formation energy determines the preferential diffusion channel of interstitials in these alloys. Similar diffusion behaviors are also observed in Fe-Cr alloys [33] and the preferential diffusion should be a general feature of

concentrated solid solutions containing chemically different elements. In fact, the relative magnitude of formation energy can be traced back to the detailed alloy structures [12]. For example, the Ni-related dumbbells have lower formation energies because of the smaller atomic size of Ni in *fcc* NiFe alloys [12]. Therefore, the accurate determination of the structural details of CSAs can help in understanding and predicting the **chemically-biased diffusion** characters. This effect is stronger at low temperature, but practically diminishes when T approaches melting (see Figs.2b, 5b and 7b). The preferential diffusion of one or two components in CSAs has a significant effect on segregation processes under irradiation: in the presence of defect sinks such as grain boundaries, voids and dislocations, the preferential aggregation of particular element will induce chemical segregation or even phase separation of the alloys. In this process, some fine precipitates could be formed, which may be beneficial to the mechanical properties of CSAs through precipitation hardening effect [34], **but the precipitation effect may also be detrimental in terms of the loss of ductility**. However, the size and distribution of the precipitates still need further studies to clarify their effect on the radiation damage evolution and strengthening under irradiation environment. **Therefore, it is difficult *a priori* to establish whether the actual effect of precipitation will be beneficial or detrimental. It is also difficult to assess whether segregation at grain boundaries will have a positive or negative effect on corrosion resistance, as the net effect will be case by case and depend on several variables; yet an effect will most certainly exist.**

5. Conclusions

Ab-initio MD simulations of interstitial atoms diffusion in NiFe, NiCo and NiCoCr CSAs reveal a sluggish diffusion in CSAs. The diffusion is mainly through one or two of constituents,

creating a specific flow of elements when interstitial diffusion takes place. This observation can be explained by the effect of chemical disorder on the formation energy of interstitials in concentrated alloys. The correlation among the chemical composition of interstitial defects, the defect formation energies and the preferential diffusion is clearly demonstrated by the examples of NiFe, NiCo and NiCoCr equiatomic random alloys. Therefore, the preferential diffusion of elements in CSAs can be understood and predicted by formation energy distributions, which are further determined by the structural details of CSAs. These results suggest preferential elemental segregation in CSAs, which will influence their phase stabilities in the radiation environment.

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Appendix A. Estimation of diffusion coefficients from atomistic simulation.

Molecular dynamics simulations produce trajectories of atoms and migrating defects in the modelled system. As the most direct approach, the diffusion coefficient D can be estimated using the Einstein relation:[35]

$$D = \frac{\langle r_s^2(t) \rangle}{2nt}, \quad (\text{A1})$$

where $r_s^2(t)$ is the square displacement (SD) of the object, t is time and n is dimensionality of the system, i.e. $n=3$ for the considered here three-dimensional diffusion of interstitial atoms. The object can be either atoms or defects, and the corresponding result is tracer or defect diffusion coefficient, respectively. In cases where modeling time is long enough, i.e. defects and atoms make enough jumps, different diffusion coefficients can be estimated directly from MD data as described in [36]. In practical modeling, one can obtain relatively long defect trajectory when many atoms are displaced, e.g. $>10^5$ interstitial jumps in [29]. However, even in this case the trajectory of individual atom is very short. Therefore, tracer and defect diffusion coefficients are usually estimated using different approaches. Usually, the atomic square displacement (ASD) is used to calculate the tracer diffusion coefficient [36]. The ASD of species s is defined as:

$$\langle R_k^2(t) \rangle = \frac{1}{N_s} \sum_{k=1}^{N_s} [\vec{r}_k(t) - \vec{r}_k(t_0)]^2, \quad (\text{A2})$$

where $\vec{r}_k(t)$ and $\vec{r}_k(t_0)$ is the instantaneous and initial position of atom k respectively and N_s is the number of atoms belonging to species s . By fitting the time dependent ASD of all or specific atoms in the simulated system to a linear function, one can get the tracer diffusion coefficients of all atoms (D^*) or a particular component s (D_s^*). To underline this method, we call it ASD tracer diffusion coefficients hereafter. By decomposing the long defect trajectory into short segments

and averaging the diffusion coefficients over all segments, one can get the defect diffusivity (D^d). The advantage of this approach lies in the possibility to estimate statistical accuracy and consequently minimize it by manipulating the number and length of trajectory segments used for the decomposition (see e.g. [36,37]).

In the case where defect trajectory is short, statistical properties can be improved by using overlapped segments to calculate the mean square displacement (MSD) [15,38] given by

$$\langle r_s^2(t) \rangle = \frac{1}{N_s N_t} \sum_{j=1}^{N_t} \sum_{i=1}^{N_s} [\vec{r}_i(t_{0j} + t) - \vec{r}_i(t_{0j})]^2. \quad (\text{A3})$$

The summation is over the number of possible time origins (N_t) and the number of atoms belonging to species s (N_s). The quantity $\vec{r}_i(t_{0j} + t) - \vec{r}_i(t_{0j})$ is the net displacement of atom i during the time span $t_{0j} - (t_{0j} + t)$. Here t_{0j} is the chosen time origin to reset the displacement accumulation. In application to MD calculated trajectories, every timestep can be used as the origin. However, the summation will include only a few timesteps near the maximum simulation time if these timesteps are used as time origins. For better statistical properties, all timesteps need to be represented equally in terms of the number of data points used to calculate the average. Following the above arguments the number of time origins is chosen to be half of the number of timesteps as in ref. [38]. Consequently, MSD is calculated between time 0 and half of the simulation time for each trajectory. The diffusion coefficient is then calculated by Eq. A1 with a linear fit to the obtained MSD-time curve. Coefficients calculated by this method are denoted as MSD tracer diffusion coefficients hereafter. In practices, after a long enough simulation time, $\langle R_k^2(t) \rangle$ and $\langle r_s^2(t) \rangle$ converge to the same value of D^* . However, due to the limited simulation time in AIMD, it is necessary to clarify the difference of D^* calculated from MSD and ASD (see Appendix C).

The diffusion coefficient calculated by Eq.A1 is related to a single defect and therefore it needs to be normalized with respect to the defect concentration. The activation energy E_a can be estimated by applying the Arrhenius law to the temperature dependence of particular diffusion coefficient D :

$$D = D_0 \exp\left(-\frac{E_a}{k_B T}\right). \quad (\text{A4})$$

After the trajectory is recorded, the position of interstitials is located at each step via the Wigner-Seitz defect analysis as implemented in Ovito [39]. In this method, the reference *fcc* lattice is divided into a series of Voronoi cells and the interstitial is identified when the occupancy of the Voronoi cells is larger than 1. The whole trajectory is then decomposed according to defect jumps as in ref. [37] and the correlation factor f_c is calculated from the mean cosine of the angle Θ between two consecutive successive jumps averaged over all pairs along the trajectory:

$$f_c = \frac{1 + \overline{\cos \Theta}}{1 - \overline{\cos \Theta}}. \quad (\text{A5})$$

This correlation factor should not to be confused with the *tracer correlation factor* that defines efficiency of atomic transport for random walk defect diffusion [35]. Averaged over a large number of jumps, f_c reflects how efficiently the defect jumps contribute to the whole defect trajectory.

Appendix B. Effects of finite supercell size.

To investigate the influence of supercell size on the calculated diffusion properties, we have compared the diffusion data obtained from a $3 \times 3 \times 3$ *fcc* supercell containing 108 lattice sites to those from a $2 \times 2 \times 2$ *fcc* supercell containing 32 sites. In the small supercell, a dense k-point mesh of $2 \times 2 \times 2$ is used. The obtained diffusion coefficients are provided in Figure 11. The

results from previous AIMD by Barnard *et al.*[15] using 32 sites are also included for comparison. Our results obtained from small supercell are in good agreement with those in [15]. It can be seen however that the diffusion coefficients increase in the larger supercell underlying the supercell size effect on diffusion modeling. This is attributed to spurious interactions between the interstitial and its periodic image when the supercell size is small.

For our calculation settings, we have analyzed the possible errors by performing static calculations on the formation energy of a [100] dumbbell defect in Ni. The result is 4.64 eV using a $2\times 2\times 2$ supercell (32 atoms) with $2\times 2\times 2$ k-points and 4.23 eV using a $3\times 3\times 3$ supercell (108 atoms) with only the Γ point, respectively. A more accurate calculation using a $4\times 4\times 4$ supercell (256 atoms) with $2\times 2\times 2$ k-points yields 4.11 eV. These calculations suggest that the uncertainty of our results is around 0.12 eV for interstitial studies. This uncertainty is in the same order of that found in a previous study [40]. For a $3\times 3\times 3$ supercell, increasing the number of k-points from Γ point to $2\times 2\times 2$ changes the formation energy to 4.06 eV. Further increase to the $4\times 4\times 4$ grid does not induce significant changes (4.07 eV). Hence the error from the k-point sampling is similar to that from the finite supercell. These errors may lead to some uncertainties in determining the precise value of diffusion coefficients, but the diffusion trend should not be affected.

Appendix C. Difference between MSD and ASD

For a long enough trajectory, the diffusion coefficient calculated from MSD and ASD should be the same. However, for short trajectories as generated in AIMD simulations, it is important to elucidate the difference between these two methods. In MSD calculations, the average is defined over both the atoms and time origins since any point during the simulation can

be considered a time origin. Thus the calculation of MSD includes the larger ensemble average, which leads to the smaller statistical error. In order to study the difference between ASD and MSD in calculating the tracer diffusion coefficient, a series of CMD calculations was performed with the Bonny2011 potential in a $3\times 3\times 3$ supercell. After allowing the system to equilibrate at 1200K for 100ps, ASD and MSD over a different time length are collected and the results are demonstrated in Figure 12. The additional average in MSD leads to smoother curve compared to ASD that is directly calculated from the instant square displacement. Regarding the tracer diffusion coefficient which is determined by the slope of ASD or MSD, the results shown in Table 5 suggest that both methods give consistent diffusivities as long as the simulation time is long enough. For the short trajectory MSD is significantly smoother but reflects stronger variations of diffusivity calculated over increasing trajectory modeling time.

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Figure 1. Tracer diffusion coefficient due to interstitial atom diffusion in pure Ni as a function of reciprocal temperature obtained from AIMD and CMD with three Bonny potentials.

Figure 2 Tracer diffusion coefficients due to interstitial atom diffusion in NiFe (a) and the ratio of partial diffusion coefficients of Ni and Fe in NiFe (b) obtained from AIMD and CMD with three Bonny potentials.

Figure 3 Fraction of the total time interstitial atom spent as Ni-Ni, Ni-Fe and Fe-Fe dumbbells during diffusion modelled by AIMD.

Figure 4 Distribution of reside time for each dumbbell structure in NiFe at 1400 K.

Figure 5 Full and partial tracer diffusion coefficients in NiCo (a) and the ratio of partial diffusion coefficient of Ni and Co (b) obtained by AIMD.

Figure 6 Fraction of the total time interstitial atoms spent as Ni-Ni, Ni-Co and Co-Co dumbbell observed in AIMD modeling.

Figure 7 Full and partial tracer diffusion coefficients of interstitial atoms in NiCoCr (a) and the ratio of partial diffusivities (b) obtained by AIMD.

Figure 8 Fraction of the total time interstitial atoms spent in various dumbbell structures in NiCoCr obtained by AIMD.

Figure 9 Correlation factors of interstitial atom jump estimated from AIMD modeling in pure Ni, NiFe, NiCo and NiCoCr.

Figure 10 The highest partial tracer diffusion coefficients calculated in different alloys compared with the tracer diffusion coefficient in pure Ni.

Figure 11 Comparison of AIMD data on trace diffusion coefficients obtained here in 108-atom and 32-atom supercells and in 32-atom supercell by Barnard *et al.*[12]

Figure 12. ASD and MSD calculated at different time intervals for interstitial atom diffusion in pure Ni using CMD with Bonny2011 potential at 1200K.

Ab initio molecular dynamics (AIMD) modeling of interstitial atom diffusion in Ni, NiFe, NiCo and NiCoCr equiatomic random alloys has demonstrated the phenomenon of *chemical anisotropy* of diffusion in concentrated alloys.

A comparison was made with the available empirical interatomic potentials for the NiFe system. Some potentials demonstrate qualitatively similar results.

Chemical anisotropy of diffusion due to interstitial atoms will lead to segregation of alloy components under irradiation.

Table 1 Arrhenius parameters for tracer coefficients due to interstitial atom diffusion in the pure Ni.

	E_a (eV)	D_0
Present	0.13	4.31×10^{-8}
Barnard <i>et al.</i> [12]	0.14	3.95×10^{-8}
Bonny2009	0.13	4.20×10^{-8}
Bonny2011	0.27	1.18×10^{-7}
Bonny2013	0.15	3.15×10^{-8}

Table 2 Parameters of an Arrhenius fit for total and partial tracer diffusion coefficients in the NiFe alloy

	Partial diffusion				Total diffusion	
	E_a^{Ni} (eV)	D_0^{Ni} (m ² /s)	E_a^{Fe} (eV)	D_0^{Fe} (m ² /s)	E_a (eV)	D_0 (m ² /s)
AIMD	0.36	9.46×10^{-8}	0.44	1.29×10^{-7}	0.39	2.14×10^{-7}
Bonny2009	1.10	8.11×10^{-7}	0.57	2.58×10^{-7}	0.59	3.21×10^{-7}
Bonny2011	0.32	7.56×10^{-7}	0.55	3.87×10^{-8}	0.34	9.52×10^{-8}
Bonny2013	0.57	1.77×10^{-7}	0.59	9.35×10^{-8}	0.58	2.70×10^{-7}

Table 3 Parameters of an Arrhenius fit for total and partial diffusion coefficients in the NiCo alloy

	E_a (eV)	D_0 (m ² /s)
Ni	0.45	1.46×10^{-7}
Co	0.30	7.47×10^{-8}
Total	0.36	1.86×10^{-7}

Table 4 Parameters of an Arrhenius fit for partial and full tracer diffusion coefficients in the NiCoCr alloy

	E_a (eV)	D_0 (m ² /s)
Ni	0.60	1.78×10^{-7}
Co	0.26	3.65×10^{-8}
Cr	0.35	5.15×10^{-8}
Total	0.35	1.53×10^{-7}

Table 5 Tracer diffusion coefficient calculated from ASD and MSD estimated over the different trajectories

Trajectory time	ASD ($\text{\AA}^2/\text{ps}$)	MSD ($\text{\AA}^2/\text{ps}$)
20ps	1.015	1.302
50ps	1.298	1.380
200ps	1.083	0.975
2000ps	1.193	1.123