

Non-empirical prediction of impurity segregation in α -Fe from first principles

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Abstract

The segregation and clustering of impurities in α -Fe were investigated by first principle density functional theory calculations. The segregation tendencies of various elements observed in reactor pressure vessels were considered and the interaction characteristics between Fe and each impurity element were estimated by mean field approximation. Stable N -atom impurity clusters were subsequently chosen to evaluate the changes in free energy for clustering. These calculations show that Cu and Mn impurities embedded in α -Fe are more stable when they are in the segregated state. Conversely, Nb and Ta are stable in the separately solute state. The present estimates provide reliable suggestions for the segregation characteristics, and the tendencies are in good agreement with the recent atom probe observations. We suggest that the segregation tendency is derived from the d -orbital interaction and that the solubility limit is not necessarily correlated with the tendency of clustering formation.

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Irradiation-induced embrittlement of low-alloy reactor pressure vessels (RPVs) is a central issue in the aging of nuclear power plants. The structural factors that contribute to hardening and embrittlement have been extensively studied using test materials¹⁻⁵. The mechanical properties of RPVs change due to aging and neutron irradiation, as neutron irradiation enhances the nucleation of lattice defects such as the highly concentrated vacancy formations and anomalous interstitial atoms. In general, most of the impurity atoms dominantly diffuse via vacancy diffusion, and the high-density vacancy condition under irradiation promotes that diffusion. The recently available three-dimensional atom probe (3DAP) allows the formation of the impurity clusters in RPVs to be directly observed under neutron and ion irradiation^{6,7} and under deformation⁸. RPV steels are generally made from low-alloy ferritic steels containing traces of impurities, and among them Cu impurities have the pronounced tendency to segregate from the matrix as confirmed using 3DAP. This segregation interferes with plastic deformation and results in the embrittlement of the material^{9,10}.

In addition to the research with test materials, atomistic simulations have been studied to investigate the singular state atomic structure under irradiation. In previous works, point defects in Fe and dilute Fe-Cu alloys and dumbbells¹¹, and the stability and mobility of self-interstitial atoms in α -Fe were investigated using first principle calculations¹². The diffusion mechanism and temperature-dependent precipitation kinetics were integrated into a Monte Carlo simulation with the embedded atom method¹³. A great number of molecular dynamics simulations of the interaction between Cu precipitation and edge/screw dislocations in α -Fe have been performed, and the dependence of the yield stress on the radius of precipitation and temperature has been investigated¹⁴⁻¹⁸. However, few satisfactory investigations of the other impurity elements in α -Fe exist, although 3DAP observations have indicated the possibility of the occurrence Mn and Ni impurity clusters as well. Therefore, a systematic investigation of the various impurity elements was considered necessary.

Although unusual defect structures in a material such as cascade damage arise under irradiation, basic information on the equilibrium state can sufficiently illuminate the segregation problem. Some excellent ways of using the vibration entropy between two phases and cluster expansions^{19,20} in conjunction with first principle analyses have been proposed and yielded acceptable results^{21,22}. These approaches are useful with specific materials and phases; however, from the perspective of the cost of calculation, it is not worth considering the various impurity elements and the corresponding possible number of configurations. In this study, the aim was to consider the various

types of impurities in α -Fe and investigate the tendency prediction of segregation and clustering. First principle density functional theory (DFT) in conjunction with the Bragg-Williams (BW) approximation^{23,24} was efficiently applied without considering actual cluster configurations. Subsequently, the change in enthalpy for clustering of the several impurity atom clusters with typically stable cluster shapes in α -Fe was evaluated, where a characteristic association between electronic states and segregation tendency was discussed.

A binary mixture was first considered to understand the segregation characteristics of an Fe-based binary system. Binary mixtures can be regarded simply as a regular solution model according to the BW approximation, and the change in free energy by mixture is given by the equation $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$, where the entropy term can be evaluated using Boltzmann statistics, provided the contribution of vibration is ignored. As the enthalpy term contributes mainly to the total free energy, the change in enthalpy is evaluated nonempirically in this study by combining the classical analysis and first principle DFT calculations. Assuming a regular solution model, the change in enthalpy is obtained from the difference in energies between the segregation limit and solid solution state using the following equation:

$$\Delta H_{\text{mix}} = N_A z \left(E_{\text{Fe-M}} - \frac{E_{\text{Fe-Fe}} + E_{\text{M-M}}}{2} \right) x_{\text{Fe}} x_{\text{M}} = W x_{\text{Fe}} x_{\text{M}}. \quad (1)$$

Here N_A is the Avogadro constant, z is the coordination number, $E_{\text{Fe-Fe}}$, $E_{\text{M-M}}$, and $E_{\text{Fe-M}}$ are the binding energies between suffixes, and x_{Fe} and x_{M} are the mixing ratios. The pressure term can be ignored when considering the aggregation system. W , the interaction parameter, is the principal factor in determining the stability of the impurities. Summing the binding energy between nearest-neighbor atoms equals the total energy of the system with the BW approximation; we assume that the total energy calculated in the DFT simulation can be distributed equally to each bond resulting in the total energy being obtained at a desirable accuracy.

The further assumption was made in the present approach that dissimilar atoms are replaced at the substitutional position. The binding energies of $E_{\text{Fe-Fe}}$ and $E_{\text{M-M}}$ were evaluated using DFT calculations prior to that of $E_{\text{Fe-M}}$. DFT calculations were then performed using the Vienna Ab initio Simulation Package (VASP)^{25,26} with the Perdew-Burke-Ernzerhof generalized gradient approximation exchange-correlation density functional from²⁷ and the projector augmented-wave method. The cutoff energy for the plane wave basis set was 500 eV. For the calculations of $E_{\text{Fe-Fe}}$ and $E_{\text{M-M}}$, $17 \times 17 \times 17$ Brillouin zone k -point sampling was selected using the Monkhorst-Pack algorithm²⁸. The lattice constant of α -Fe was found to be 2.8335 Å and the total energy is directly

correlated with $E_{\text{Fe-Fe}}$. The binding energies between impurities were obtained similarly from the bcc phase at the same lattice constant as the stable α -Fe matrix. In this study, various kinds of transition metals of V, Cr, Mn, Co, Ni, Cu, Ni, Cu, Zn, Nb, Pd, Ag, Ta, and some representative elements were taken to be the impurities in α -Fe, because most of them are well-known impurities in reactor pressure vessels. Subsequently, the binding energies between α -Fe and the impurity elements were investigated. The simulation cell was a $3 \times 3 \times 3$ bcc lattice that included fifty-three Fe atoms and an impurity atom. Moreover, $7 \times 7 \times 7$ Brillouin zone k -point sampling was used, and the fully relaxed configurations were obtained by the conjugate gradient (CG) method with a convergence condition of $0.02 \text{ eV}/\text{\AA}$. The interaction energy between α -Fe and impurity $E_{\text{Fe-M}}$ is derived from both the total energy of the intended system E^{tot} and the binding energy of matrix atoms $E_{\text{Fe-Fe}}$ and is expressed by the following equation:

$$E_{\text{Fe-M}} = \{E^{\text{tot}} - z(N/2 - 1)E_{\text{Fe-Fe}}\}/z. \quad (2)$$

Here N is the total number of atoms in the simulation cell. The definitional Eq. (2) was used to evaluate the interaction parameter. Although the regular solution approximation includes essentially inevitable error, the long-distance contribution to the nearest neighbor can be summarized using $E_{\text{Fe-M}}$, and thus the effect of the impurity element is sufficiently considered.

As impurities are first segregated at the lattice site of α -Fe, the interaction parameter is useful in predicting the early-stage nucleation process. The equivalent binding energies of Fe and the impurities and resulting interaction parameters were calculated using DFT and are summarized in Table I, where the total number of atoms is fifty-four and the coordination number is eight in consideration of the bcc phase. It is confirmed from Table I that the interaction parameters of Cu and Mn are positive. The results imply that these impurities tend to segregate from the Fe matrix. Conversely, some transition metals such as Nb, Mo, and Ta and all representative elements are negative values with large absolute values, thus predicting that these impurities are difficult to segregate.

To validate the above estimation, the change in free energy was considered in the case that randomly distributed impurities segregated and made specific clusters. Classical nucleation theory was introduced to evaluate the free energy for clustering. According to nucleation theory, changes in free energy are expressed by the enthalpy that includes the volumetric and interfacial terms and the entropy term given by the following equation: $\Delta G = (\Delta H_V + H_S) - T\Delta S$. In reality, however, it is simply impractical to evaluate both the volumetric and interfacial terms separately because

TABLE I: Equivalent binding energies of Fe, impurities, and Fe-impurity calculated at bcc phase at the lattice constant of most stable α -Fe ($a_0 = 2.8335 \text{ \AA}$) and interaction parameters of the Fe-M binary system.

Mater.	Binding energy in bcc phase of Fe		Interaction parameter
	$E_{\text{Fe-Fe}}, E_{\text{M-M}}$ (eV)	$E_{\text{Fe-M}}$ (eV)	W/Nz (eV)
Fe	-2.08	-	-
V	-2.21	-2.26	-0.12
Cr	-2.38	-2.25	-0.017
Mn	-2.22	-2.13	0.015
Co	-1.75	-1.94	-0.030
Ni	-1.34	-1.72	-0.014
Cu	-0.92	-1.41	0.084
Zn	-0.19	-1.18	-0.023
Nb	-1.76	-2.31	-0.39
Mo	-2.32	-2.40	-0.20
Pd	-1.00	-1.63	-0.093
Ag	-0.20	-1.15	-0.013
Ta	-2.12	-2.56	-0.46
Al	-0.72	-1.60	-0.20
Si	-1.14	-1.87	-0.26
P	-1.11	-1.84	-0.25
S	-0.62	-1.53	-0.18

various types of cluster shapes need to be considered. Additionally, the interfacial energies of a variety of planes cannot be calculated. If the generality of the analytical theory is sacrificed, the change in enthalpy for clustering can be replaced by the sum of both volumetric and interfacial contributions on the assumption that the cluster shape is preliminarily presented and expressed by the following equation: $\Delta H_V + H_S \Rightarrow \Delta H_C^{N_c}$, where N_c is the number of impurity atoms of the intended specific cluster. In this study, impurity clusters including two-six impurity atoms were considered, where comparatively stable shapes in the bcc phase were selected. DFT calculations were performed to evaluate the heats of solution of impurity clusters under the same conditions as

the above calculation. Atomic relaxation was implemented using the CG method with the above-mentioned convergence condition. Thus, the heats of solution of both a single impurity atom and N -atom cluster were calculated. Therefore, the assumption can be made that the change in enthalpy for clustering can be approximated using the heats of solution of both the single impurity atom E_{HoS} and the intended N -atom cluster $E_{\text{HoS}}^{N_C}$ using the following equation:

$$\Delta H_C^{N_C} \simeq E_{\text{HoS}}^{N_C} - N_C E_{\text{HoS}}. \quad (3)$$

Here N_C is the number of impurities. Assuming that the heats of solution in an infinite matrix are calculated, Eq. (3) becomes a true equality. Thus, the changes in enthalpy for clustering can be evaluated. The atomic configurations of selected N -atom clusters and their changes in enthalpy are shown in Fig. 1 (a) and (b), respectively. It is found from this figure that the $\Delta H_C^{N_C}$ for clusters composed of Cu, Ni, Mn, Zn, and Ag are negative, which shows that these reactions are exoergic, and thereby reveals that all these impurities prefer to segregate from the matrix to make clusters. Conversely, the changes in enthalpy of the other impurity elements are positive, which means that these elements resist segregation. This suggestion is close to previously obtained tendencies based on the BW approximation. Clusters composed of Cu, Mn, and Ni were observable using the recently available 3DAP⁷, although Mn and Ni are known as comparatively soluble elements. Contrariwise, Nb and Ta clusters have not been detected. Our predictions agree rather well with the experimental observation, and therefore it is particularly worth noting that the solubility limit estimated from the phase diagram of Fe-based binary alloys²⁹ does not necessarily correspond to the segregation characteristics.

The clustering of impurities in α -Fe is determined by the binding characteristics; that is, the electronic interaction between the d -electron of α -Fe and the outer electron of the impurity element. The local density of states (DOS) of Cu and Nb impurities embedded in α -Fe are shown in Fig. 2, which are taken as the typical cases of segregation and antisegregation elements. Here the local DOS patterns of the nearest neighbor Fe atom to the impurities and those of single-component Cu and Nb at bcc phase are drawn for comparison. It is found in Fig. 2 (a) that the occupied or closed d -shell structure of Cu produces a weak interaction with the matrix element. On the other hand, in Fig. 2 (b), the local DOS of Nb changes shape dramatically when it is embedded in α -Fe. A strong adhesive interaction is observed in the range of -4.0 to -2.0 eV of up-spin state due to the unoccupied d -electron of Nb. Finally, a sequence of electronic state calculations presents the reliable prediction for segregation and clustering and supply a quantitative

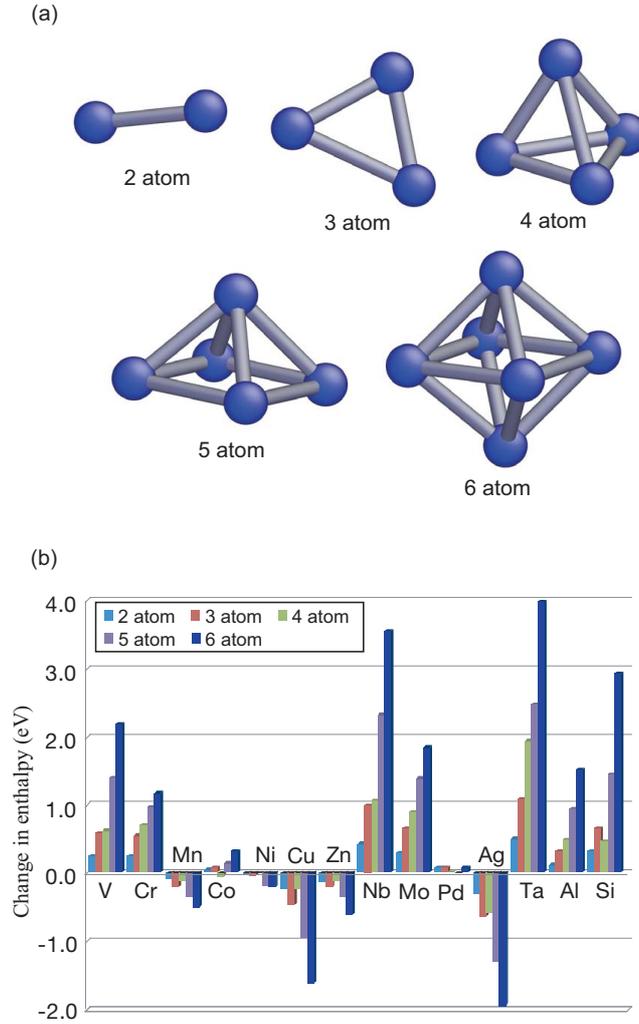


FIG. 1: (Color online) (a) Selected cluster shapes of two-six atom clusters. (b) Enthalpy changes from the isolated impurity to the segregated N -atom clusters evaluated by Eq. (3).

underpinning.

In summary, the segregation and clustering of various types of impurities in α -Fe were predicted using DFT calculations in conjunction with analytical models. Interaction characteristics based on the BW approximation were evaluated using equivalent binding energies between α -Fe and the impurities. The interaction parameters of Cu and Mn are extremely large positive values, which indicate the tendency to segregate from the α -Fe matrix when compared with other impurities. Several clusters including two-six impurity atoms were then selected, and the enthalpy changes for clustering were evaluated, which is represented by the heats of solution of both a single impurity and a N -atom cluster. Enthalpy changes of clustering composed of Cu, Ni, Mn, Zn, and Ag are negative, which reveal that they prefer to make clusters. These tendencies agree well with

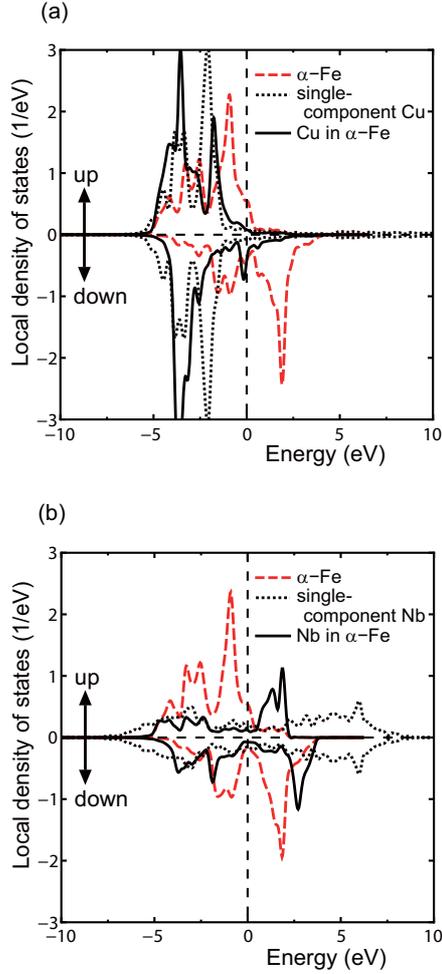


FIG. 2: (Color online) Local DOS of the typical segregated and nonsegregated impurities of (a) Cu and (b) Nb embedded in α -Fe, where the local DOS of the nearest neighbor Fe atom and those of single-component Cu and Nb at bcc phase are drawn.

the 3DAP observation. These segregation tendencies are derived from the d -orbital interaction with the Fe matrix, and therefore our results indicate that the solubility limit in the matrix cannot necessarily be correlated with clustering. The physically meaningful predictions for segregation characteristics can be estimated.

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