

Vacancy Mechanism of High Oxygen Solubility and Nucleation of Stable Oxygen-Enriched Clusters in Fe

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First-principles studies identify a vacancy mechanism underlying the unusually high O solubility and nucleation of stable O-enriched nanoclusters in defect-containing Fe. Oxygen, confined as an interstitial, shows an exceptionally high affinity for vacancies, an effect enhanced by spin polarization. If vacancies preexist, the O-vacancy pair formation energy essentially vanishes, allowing the O concentration to approach that of the vacancies. This O-vacancy mechanism enables the nucleation of O-enriched nanoclusters, that attract solutes with high O affinities (Ti and Y) and strengthen Fe-based alloys.

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A high density of stable nanoclusters has been recently identified in Fe-based alloys processed by mechanical alloying [1–5]. Atom probe analyses have found that these clusters, with diameters 2–4 nm and highly diffusive interfaces, are distinctly enriched in O, as well as Ti and Y alloying additions [1–5]. Such alloys have excellent strength and hardness at both room and elevated temperatures. Moreover, long-term creep tests have found that the clusters reduce the creep rate at 650 °C–900 °C by 6 orders of magnitude [6], testifying to a major breakthrough in the design of Fe-based alloys. These clusters are self-assembled and ultrastable, with no coarsening even after 14 000 h creep studies at 800 °C, or extended heat treatments at 1300 °C [4]. The unusually high stability of these clusters is surprising given that nanophase materials are typically metastable in nature because of rapid coarsening at elevated temperatures. These nanoclusters are supersaturated with O, whose concentration can approach ~40 at. % [1–5]. The average O content of the Fe matrix, ~0.15 at. % O [1–5], is also significantly higher than the expected equilibrium O solubility in Fe [7]. Such observations suggest that these nanoclusters represent a novel material state resulting from very stable binding among the constituent elements. As discussed later, we find that these nanoclusters can accommodate high vacancy concentrations. The technological consequences are great: nanocluster-strengthened alloys have an extended temperature range of application and can potentially resist the detrimental effects of excessive irradiation-induced vacancies (e.g., in reactor materials). Thus, it is important to understand the mechanisms leading to the formation and stability of these nanoclusters.

In this first-principles study, we investigate the Fe:O interactions in α -Fe, identifying mechanisms that explain the high O solubility and the initial nucleation stage of the observed O-enriched nanoclusters. We also compare the interactions of O in Fe with those of C and N in Fe (C and N interstitials in Fe have been studied extensively by first-principles in references [8–11]) in order to identify the

bonding characteristics that differentiate them. We find that the binding of O in Fe is rather weak compared to C and N, such that O has a relatively stronger affinity for vacancies. In fact, O-vacancy binding energies are several times greater than that of corresponding C- and N-vacancy structures. A magnetism-induced O confinement is also identified as one of the significantly contributing sources to this unusually strong O-vacancy binding. Most surprisingly, although O has a very high formation energy (and low solubility) in defect-free Fe, the formation energy of the O-vacancy (O:V) pairs becomes vanishingly small if the vacancies are present as preexisting defects in Fe (thus allowing the O concentration to approach that of the vacancies). It is emphasized that this type of nanocluster formation in Fe-based alloys is observed only upon mechanical alloying, a process known to create a high concentration of lattice vacancies. Ti and Y alloying additions in the Fe lattice also bind strongly with O:V pairs. Our results suggest that defects and solutes that have high formation energies individually can collectively form a bound state of low energy and high stability. Thus, we identify vacancies as the most critical alloying element in the formation and stability of these nanoclusters.

Our calculations employed the ultrasoft pseudopotential [12] approach within the generalized gradient approximation (GGA) [13]. The spin-polarized local density equations were solved using the Vienna *ab initio* simulation package (VASP) [14] and a plane-wave energy cutoff of 400 eV. Calculated bulk and defect properties of Fe agree well with other works [8–10]; however, sensitivities were further checked using the projector augmented wave (PAW) [15] approach and the PBE-GGA [16]. The O binding energy, Fe-vacancy formation energy, and O-vacancy binding energy in Fe from each model are all within 0.1 eV. A 54-atom supercell representation of the Fe matrix gives convergence (according to tests with a 128-atom supercell) to within 0.1 eV for the energies of O binding and vacancy formation.

We find that in defect-free Fe, oxygen binds preferentially at an octahedral interstitial site (as also reported for C and N interstitials [8–11]). In order to understand the different effects of O and C (or N), we first address the binding energy of an interstitial I in the Fe host, defined as

$$E_b(\text{Fe}/I) = E(\text{Fe}^n/I) - nE(\text{Fe}) - E(I). \quad (1)$$

Here $E(\text{Fe}^n/I)$ is the energy of an n -atom Fe host with an interstitial I , $E(\text{Fe})$ is the energy per atom of a defect-free Fe host and $E(I)$ is the energy of an isolated I atom. The calculated binding energy for O is -4.01 eV, while those for N and C are considerably larger, -5.37 eV and -7.11 eV, respectively. This raises a question as to the role of weakness of the O-Fe interaction in the nanocluster formation.

Spatial differences in the O-Fe bonding compared to that of C and N are apparent in the charge density distributions shown in Fig. 1, and they are consistent with the binding energy trend. The differential charge density is defined as the difference between the charge density of (1) the interstitial-containing Fe system and (2) the superposition densities of the Fe host and the free interstitial. The systematic change in bonding of C, N, and O is largely one of increasing ionicity relative to covalency in progressing from C to O, as a consequence of the increasing anion electronegativity. The increasing population of p orbitals for atoms from C to O is reflected by the strong p_z^2 density change on C contrasted with the near-spherical distribution of charge increase on the O site (Fig. 1). Thus, the O charge is spatially confined (localized) and weakly polarized, compared with the C and N charges that exhibit significant delocalization and polarization in the [001] direction. The decrease in the interstitial-host binding energies with lower covalency $\text{C} \rightarrow \text{O}$ is large but fairly uniform and is consistent with the density shifts. These trends in bond character explain the relative weakness of the O-Fe interaction.

Each interstitial (C, N, and O) is found to attract and bind vacancies in the Fe host. This has been reported earlier [8,11] for N and C. As a result of the weak bonding of O in Fe, O exhibits the strongest vacancy attraction among these three interstitials, with an exceptionally large binding energy that defines a highly stable O:V pair.

Surprisingly, we find that an O interstitial binds not only a $\frac{1}{2}$ [001] nearest-neighbor (NN) vacancy (forming an O:V pair) with a very large binding energy of -1.45 eV, but also a $\frac{1}{2}$ [110] next nearest-neighbor (NNN) vacancy with a sizable energy of -0.60 eV. Furthermore, each O:V pair can bind an additional vacancy; if such a vacancy is a NN to O, the binding energy between an O:V pair and the second vacancy is large, -0.85 eV; moreover, if the second vacancy is a NNN to O, the binding is still appreciable, -0.35 eV. By comparison, N and C bind NN vacancies more weakly with energies of -0.63 eV and -0.40 eV, respectively, (consistent with results of Ref. [8]), and only N shows stable binding with a NNN vacancy (-0.11 eV).

For O in an interstitial octahedral site without NN vacancies, there is strong spatial confinement due to the very short Fe-O bond length (1.81 Å) along [001]. However, a significant charge buildup at the O site suggests that magnetism of the Fe lattice actually plays a role in confining the local O charge. This is made clear in Fig. 2(a) where the difference between spin-polarized and spin-unpolarized total charge densities is shown for interstitial O in the octahedral site of defect-free Fe (the atomic positions for both calculations correspond to those of the fully relaxed spin-polarized calculation). A sizeable amount of charge that exhibits strong axial confinement is evident with localization in the core region of the O atom. This results as the magnetism of the host lattice causes a contraction of the O density, reducing the amount of O charge in the interstitial region. Now, with creation of a NN vacancy, the O charge confinement is alleviated by electron delocalization into the newly-created volume [see Fig. 2(b)]: as a result, the O-vacancy binding is greatly enhanced, as indicated by a displacement of the O atom by 0.23 Å towards the vacancy. The importance of magnetism for this unusual effect is confirmed by calculating the O-vacancy binding energy in a hypothetical nonmagnetic Fe matrix. With atomic positions fixed at the corresponding spin-polarized case, non-spin-polarized calculations reveal that the binding of O with its NN Fe-vacancy is much weaker (-0.35 eV).

Even though the probability of an O atom having two NN Fe vacancies is low, this configuration serves to further

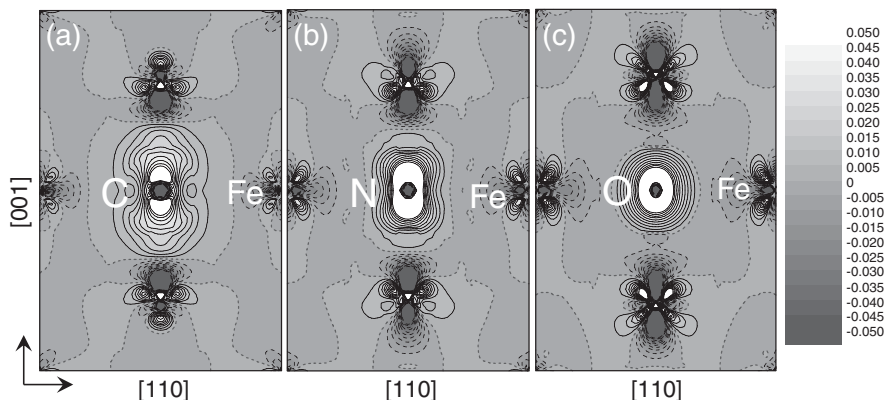


FIG. 1. Differential charge densities in units of $e/(\text{bohr})^3$ in the (110)-plane for (a) C, (b) N, and (c) O in an octahedral interstitial site of α -Fe.

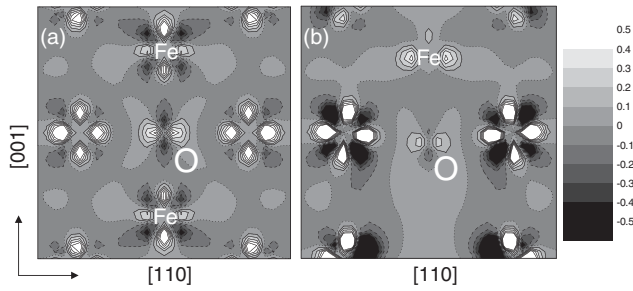


FIG. 2. Difference in the total charge densities in units of $e/(\text{bohr})^3$ between the spin-polarized and spin-unpolarized calculations for O in (a) defect-free Fe-lattice, and (b) Fe-lattice with a vacancy NN to O. Charge density localized on the O site is spin-confined in defect-free Fe (a); however, it expands considerably over the volume of a NN vacancy (b) with little spin-induced localization.

distinguish the behavior of O from that of N and C. The binding energy of O with two NN Fe vacancies is large, -2.30 eV, compared with the corresponding energies for N and C, -1.00 eV and -0.80 eV, respectively. The physical reason for the abrupt change in the binding energies from C to O is revealed in Fig. 3, which shows dramatic differences in the differential charge densities in the (110) plane for C, N and O with two NN Fe vacancies. The charge densities of both N and C in Fe show a strong change in directionality upon creating two NN vacancies, reorienting from the [001] direction (for defect-free Fe) and expanding along [110], as covalentlike bonds with the NNN atoms strengthen in the absence of nearest neighbors along [001] (compare Figs. 1 and 3). In contrast with C and N, O shows no charge depletion along the [001] direction; rather, the density remains nearly spherical.

How are these differences in bonding related to the observed greatly enhanced O solubility in the Fe-matrix? In the absence of defects, the low solubility of O in Fe at high-temperature is a result of the reaction $\text{Fe}/\text{O} \rightarrow \text{Fe} + \text{FeO}$, leading to the precipitation of FeO. The formation energy of O in defect-free Fe can be calculated from

$$E_f(\text{Fe}/\text{O}) = E(\text{Fe}^n/\text{O}) - E(\text{FeO}) - (n-1)E(\text{Fe}). \quad (2)$$

Here $E(\text{FeO})$ is the energy of FeO per formula unit. Our calculated O formation energy in defect-free Fe is quite high, 1.45 eV, that coincidentally equals the negative of the binding energy of an interstitial O with a NN vacancy. Thus, if lattice vacancies preexist in the host, the formation energy of the O:V pair given by

$$E_f(\text{Fe}/\text{O:V}) = E(\text{Fe}^{n-1}/\text{O:V}) - E(\text{FeO}) - E(\text{Fe}^{n-1}/\text{vac}) + E(\text{Fe}) \quad (3)$$

becomes nearly zero as the strong O-vacancy binding substantially lowers the effective O formation energy. In Eq. (3), $E(\text{Fe}^{n-1}/\text{O:V})$ and $E(\text{Fe}^{n-1}/\text{vac})$ are the energies of the $(n-1)$ -atom host with an O:V pair and with a vacancy, respectively. Note that, in Eq. (3), the reference system is the Fe lattice with vacancies rather than defect-free Fe. In other words, a high O solubility requires O:V pair formation (with vacancies preexisting). Alternatively, one can view an O:V pair as formed by a relaxed substitutional O atom (O_s) from a lattice site. In this case, the formation energy of O_s in Fe can be expressed as

$$E_f(\text{Fe}/\text{O}_s) = E(\text{Fe}^{n-1}/\text{O:V}) - E(\text{FeO}) - (n-2)E(\text{Fe}). \quad (4)$$

The resulting energy is 1.95 eV. Since the formation energy of an isolated vacancy in Fe is calculated to be 1.95 eV also, it follows that the formation energy of an O:V pair essentially vanishes if vacancies preexist.

We also note that the O-vacancy binding significantly reduces the mobility of O in Fe. From our calculations, the migration barrier of an octahedral O interstitial in Fe (0.60 eV) is about the same as the migration barrier of a vacancy. However, once the O:V pair is formed, the O:V pair remains bound and migrates together in a two-stage process. In the first stage, O is separated from its NN vacancy by the migration of a NNN Fe atom into the vacant site; in the second stage, O migrates almost spontaneously to bind with the vacancy at the former Fe site. The calculated O:V migration activation energy (1.55 eV) is, within the accuracy of our calculations, almost entirely due to the migration barrier associated with the first stage of the O:V

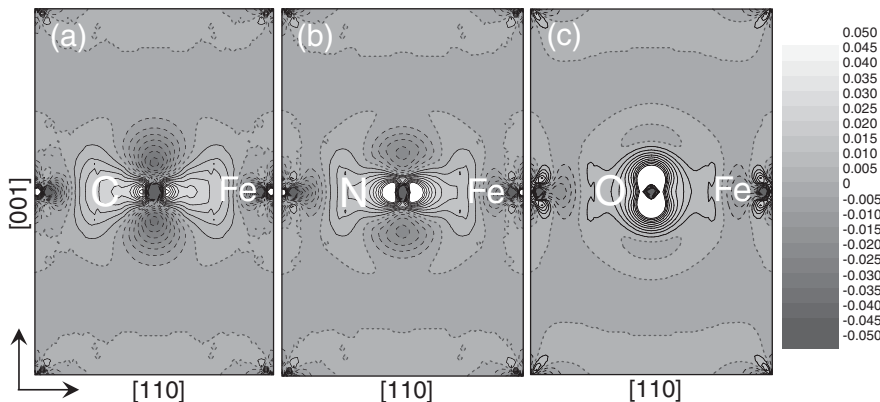


FIG. 3. Differential charge densities in units of $e/(\text{bohr})^3$ in the (110)-plane for (a) C, (b) N, and (c) O in the presence of two NN vacancies along [001] in Fe.

migration. The O:V migration barrier is clearly less than 2.05 eV, the energy required for the dissociation of an O:V pair and migration of O in the form of an isolated interstitial.

Experimentally, the compositions of O-, Ti-, and Y-enriched nanoclusters are found to be ~ 40 at. % Ti, ~ 10 at. % Y and ~ 40 at. % O with Fe comprising the balance [1–5]. The O concentration in these clusters is quite high. In order for nucleation of the nanoclusters on the Fe lattice to occur, the binding energy of an O atom [$E_b(\text{O})$] in the cluster has to be lower than the heat of formation of the TiO_2 oxide phase (relative to the energy of substitutional Ti in Fe). We note that there is a large energy difference (3.7 eV) between $E_b(\text{O})$ in defect-free Fe and the heat of formation (per O) of TiO_2 . However, we show in the following that vacancies play a pivotal role in reducing this energy difference.

Here we focus on the initial nucleation stage of the nanoclusters. With O atoms (in O:V pairs) located near the interstitial octahedral sites, energy minimization shows that their neighboring $\frac{1}{2}[110]$ lattice sites are energetically available sites for Ti solutes and neighboring $\frac{1}{2}[112]$ lattice sites are energetically preferred sites for Y solutes. We find that $E_b(\text{O})$ in O:V increases (i.e., becomes more negative) by as much as 3.2 eV from that in defect-free Fe as the neighboring $\frac{1}{2}[110]$ Fe atoms are progressively replaced by Ti atoms; this follows since Ti has a higher affinity for O than Fe. The existence of a Ti-vacancy attraction also contributes to this increase in $E_b(\text{O})$.

The interaction between interstitial O atoms in the absence of vacancies is found to be repulsive if their distance is less than a lattice constant a . However, an attractive interaction between O interstitials, even at $0.7a$ separation, can be achieved if O is present in the form of O:V pairs. As mentioned already, a unique feature of the O:V pair in Fe is that it can attract an additional vacancy, not only in [001] directions, but also in [110] directions. Using experimental observations that the O content in the nanoclusters is ~ 40 at. % [1–5] (corresponding to having about one O atom per unit cubic cell), we obtain a further increase in $E_b(\text{O})$ by approximately 0.4 eV due to the interaction between O:V pairs in the presence of Ti (in a pair-interaction approximation).

By considering the effects of Ti, O and vacancies surrounding an O atom in an O:V pair, we have shown above that the increase of $E_b(\text{O})$ can be as large as 3.6 eV. This increase of $E_b(\text{O})$ is surprisingly close to the energy difference (3.7 eV) between $E_b(\text{O})$ in defect-free Fe and the heat of formation of TiO_2 . Nevertheless, it is likely that the TiO_2 phase will form in the absence of ternary additions. On the other hand, the small difference between $E_b(\text{O})$ in the cluster and the heat of formation of TiO_2 raises the possibility for the stabilization of clusters in Fe with further alloying additions. Indeed, our calculations show that small additions of Y further increase $E_b(\text{O})$, in turn en-

abling the formation of nanoclusters instead of TiO_2 . We note that the interaction between O and Y in Fe has to be mediated by vacancies; without vacancies, the interaction between O and Y in Fe is found to be repulsive.

We stress once again that the fundamental alloy feature that differentiates these nanoclusters from equilibrium compound phases, such as oxides, is that vacancies play an indispensable part in their structure and stability. Most compound phases can accommodate vacancies on the lattice sites under equilibrium conditions; however, the concentration of vacancies is usually very small. By contrast, the vacancy concentration in these nanoclusters is very high, and the binding between vacancies and interstitial O atoms is central to the structure and stability of the Y-, Ti-, and O-rich nanoclusters in the Fe-based alloys. The formation energy of these clusters can become lower than that of stable oxide phases, since the solute Ti and Y atoms form strong bonds with both oxygen and vacancy structures. When present as point defects (vacancies, solute atoms and interstitial O atoms), each of these elements individually has a high formation energy, indicating little solubility in the Fe lattice. However, we have found that nanoclusters of these elements with vacancies have very low formation energies, such that high solubilities can be attained. Thus, the stability of these nanoclusters is a consequence of the fact that point defects that have high formation energies individually can collectively form a bound state system of low energy and high stability.

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