Inert gas bubbles in bcc Fe

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**Abstract**

The properties of inert gas bubbles in bcc Fe is examined using a combination of static energy minimisation, molecular dynamics and barrier searching methods with empirical potentials. Static energy minimisation techniques indicate that for small Ar and Xe bubbles, the preferred gas to vacancy ratio at 0 K is about 1:1 for Ar and varies between 0.5:1 and 0.9:1 for Xe. In contrast to interstitial He atoms and small He interstitial clusters, which are highly mobile in the lattice, Ar and Xe atoms prefer to occupy substitutional sites present in the lattice. Ar and Xe atoms are much harder to form than bubbles of He and that such gases produced in a nuclear reaction would more likely be dispersed at substitutional sites without the help of increased temperature or radiation-driven mechanisms.

1. Introduction

Ferritic and martensitic steels are candidate materials for use in nuclear reactors [1,2]. The transmutation-created inert gas, especially He, plays an important role in the microstructural evolution of these steels under neutron irradiation. In a previous paper [3] the mechanisms by which He in a perfect body-centred-cubic (bcc) Fe lattice, can agglomerate into bubbles was discussed. It was shown that small He interstitial clusters are highly mobile but become effectively pinned with the emission of Fe interstitials when the clusters contain 5 or more He atoms. Small bubbles up to around 1.5 nm in diameter can easily form at room temperature from such seed points but larger bubbles are more difficult to form by diffusion alone due to the induced strain in the bcc lattice which increases the energy barriers for diffusion towards the bubbles whilst reducing them in a direction away from the bubbles. Subsequent bubble enlargement can then only occur either through increased temperature or by radiation induced mechanisms which increase the number of vacancies in the bubble and reduce the lattice strain. Emission of interstitial loops from such a bubble was not observed in molecular dynamics simulations.

Since He is not the only inert gas to occur as a result of nuclear reactions and in addition Ar and Xe are often used in ion bombardment experiments, it is important to understand if similar mechanisms can also result in bubble growth for these gases. In this paper bubbles of Ar and Xe in bcc Fe are therefore investigated.

There is much less experimental evidence for the presence of bubbles of Ar or Xe either as a result of nuclear reactions or through energetic inert gas bombardment. Microstructural evolution of P92 ferritic/martensitic steel irradiated by Ar$^+$ ion beams at doses from 0.6 to 230 displacements per atom (dpa) at room temperature was investigated with a conventional transmission electron microscope technique by Jin et al. [4]. The work investigated the effect of irradiation on embedded carbide particles which became partly amorphous at an irradiation dose of 2.3 dpa and were almost completely amorphous at the dose of 11.5 dpa. Although not specifically mentioned in the paper, the micrographs contained no evidence of Ar bubble formation.

However Klimenkov [5] showed clear microscopic evidence for Ar bubbles in oxide dispersion strengthened (ODS) steel where the bubbles appear at the interface between the ODS particle and the surrounding matrix. Here the smaller bubbles were measured to have a concentration of 15–18 Ar atoms per cubic nanometre. In this case the ODS material was prepared by ball milling in an argon...
atmosphere so that the argon was incorporated into the bulk materials during the preparation process.

Thus, although such bubbles have been observed, it is not clear under what circumstances they can form. This paper therefore attempts to address the issue. The techniques used here are the same as in Ref. [3], namely empirical potentials, static energy minimisation, molecular dynamics (MD) and barrier searching.

### 2. Methodology

For simulating the gas-vacancy clusters in the bcc iron system, we use a Lennard-Jones potential [6] for the Ar–Ar and Xe–Xe interaction, a ZBL potential [7] for Ar–Fe and Xe–Fe and the Ackland-Mendelev potential for Fe–Fe [8]. Molecular dynamics simulations are carried out using a code LBOMD which has been developed in our group and used over a number of years. Energy barriers are calculated either using the Nudged Elastic Band (NEB) Method [9] when the initial and final states are known or by barrier searching using the dimer or Relaxation and Translation (RAT) method [10,12]. The RAT method is a modification of the ART method developed by Mousseau and others [11].

### 3. Formation energies

The formation energies of interstitial and substitutional inert gas atoms calculated using conjugate gradient minimisation are given in Table 1. The He data is taken from Ref. [3] for comparison. Here the formation energy of the substitutional site is defined to be the difference in energy between a perfect bcc Fe lattice with the gas atom at infinity and the lattice of the same number of Fe atoms with the substitutional atom added. Thus

\[
E_{\text{sub}}^{\text{gas}} = E_{\text{sub}}^{\text{ref}} - N_{\text{Fe}}^0 E_{\text{Fe}},
\]

where \(E_{\text{sub}}^{\text{gas}}\) is the formation energy of the gas substitutional atom; \(E_{\text{sub}}^{\text{ref}}\) is the energy of the system with the gas atom added; \(E_{\text{Fe}}\) is the cohesive energy of Fe and \(N_{\text{Fe}}^0\) is the number of Fe atoms in the reference system.

The interstitial formation energies are similarly defined and refer to the difference in energy between a perfect Fe lattice and one that has the interstitial gas atom inserted. In all cases the substitutional site is favoured but there is a much larger difference in energy for Ar and Xe compared to He.

The formation energies of the gas-vacancy clusters \(\text{Ar}_n\text{V}_m\) and \(\text{Xe}_n\text{V}_m\), where \(n\) is the number of inert gas atoms and \(m\) refers to the number of missing Fe atoms, (note that the number of Fe vacancies is not necessarily the same as the number of inserted gas atoms) are calculated using a Monte Carlo algorithm, which was introduced in Ref. [3]. In brief the method starts by creating a void with \(m\) missing Fe atoms, removing the atoms one at a time by choosing the Fe atom with the largest potential energy in the system. The energy is minimised at each step. The \(n\) He atoms are then added and the system minimised by using a combination of the Metropolis Monte Carlo method to alter the He positions followed by conjugate gradient minimisation.

The formation energy of a gas-vacancy complex is defined as the difference in total energy between a crystal containing the defect and a perfect crystal of the same number of Fe atoms with the corresponding number of gas atoms in their lowest energy structure.

\[
E_f = E_b + (n - m)E_{\text{vac}} - N_{\text{Fe}} E_{\text{Fe}} - nE_{\text{sub}}^{\text{gas}},
\]

where \(E_f\) is the formation energy, \(E_b\) is the energy of the lattice containing the bubble; \(E_{\text{vac}}\) is the formation energy of a single

### Table 1

| Gas species | Substitutional formation energy | Tetrahedral formation energy | Octahedral formation energy |
|-------------|--------------------------------|----------------------------|-----------------------------|
| He          | 3.76 eV                        | 4.38 eV                    | 4.47 eV                     |
| Ar          | 12.20 eV                       | 16.82 eV                   | 17.61 eV                    |
| Xe          | 15.45 eV                       | 20.15 eV                   | 20.43 eV                    |

Fig. 1. The formation energy as a function of the number of argon atoms for different sizes of \(\text{Ar}_n\text{V}_m\) clusters.
vacancy in an otherwise perfect bcc Fe lattice, defined as follows;

\[ E_{\text{vac}} = E(v, N-1) - (N-1)E_{\text{Fe}}, \]  

(3)

where \( E(v, N-1) \) is the energy of the lattice containing one vacancy and \( N-1 \) is the number of Fe atoms in the system. \( N_{\text{Fe}} \) is the number of Fe atoms in the lattice containing the bubble.

Fig. 1 shows the formation energy of the \( Ar_v V_m \) clusters in bcc Fe at 0 K. Each curve is evaluated with a fixed number of vacancies, which implies that all the bubbles on an individual curve have preformed vacancies before the Ar is inserted. To ensure the results can be compared on a similar scale, the figure shows the formation energy per vacancy. It is clear that there is an optimal (lowest formation energy per vacancy) Ar-to-vacancy ratio for each curve. The optimum bubble size is given by the minima on the curves in Fig. 1. It can be seen that the optimum ratio is around 1:1. Further, each curve stops at the final point because the bubble is no longer stable to hold more argon with the given number of vacancies; in other words, adding extra argon will cause the bubble to push the neighbouring Fe atoms into interstitials thus adding more vacancies into the bubble. This is shown schematically for the 5 vacancy case in Fig. 2.

The 1:1 ratio works out at about 14 Ar per cubic nanometre of material similar to the experimental values measured by Klimenkov [5]. A similar result also occurs for the formation energies of \( Xe_v V_m \) clusters. In this case the optimal ratio varies between about 0.5:1 to 0.9:1 as shown in Fig. 3.

4. Molecular dynamics simulations and energy barrier calculations

Previously it was shown [3,13] that if randomly placed interstitial He atoms were inserted into a perfect bcc lattice at elevated temperature, the He rapidly diffused to form small bubbles by pushing out Fe atoms. This rapid diffusion is because the energy barrier for interstitial diffusion is 0.06 eV as shown in Table 2. This is much lower than the barrier for the He to become substitutional and eject an Fe interstitial calculated as 6.8 eV. In the case of randomly inserted Ar and Xe interstitials this does not happen. MD simulations at 500 K show that the atoms become substitutional over a 1 ns time scale producing Fe dumbbell interstitials. This only occurs with He when the cluster reaches a size of 4 or 5 He interstitial atoms. Small He clusters up to those sizes are mobile in the

![Fig. 2. Illustration of the effect of adding an Ar atom to an \( Ar_v V_3 \) bubble. On adding an additional Ar atom, a Fe split interstitial is spontaneously formed.](image)

![Fig. 3. The formation energy as a function of the number of xenon atoms for different sizes of \( Xe_v V_m \) clusters.](image)

| Gas species | Interstitial–interstitial barrier | Interstitial-substitutional barrier | Substitutional-interstitial barrier |
|-------------|----------------------------------|-----------------------------------|-----------------------------------|
| He          | 0.06 eV                          | 6.8 eV                            | 7.4 eV                            |
| Ar          | 0.3 eV                           | 0.07 eV                           | 1.4 eV                            |
| Xe          | 0.5 eV                           | 0.15 eV                           | 1.8 eV                            |
The reason why Ar and Xe atoms become substitutional can be seen from Table 2 which shows that the energy barriers, calculated using the NEB method, for interstitial Ar or Xe atoms to become substitutional, are much lower than those involving diffusion to another interstitial site. The reverse barriers for Ar or Xe substitutional atoms to become interstitial are much higher at 1.4 eV and 1.8 eV respectively.

To give some idea of the jump frequency with these large barriers we can use the Arrenhius equation.
\[ \nu = n_0 \exp(-E/kT) \]

where \( E \) is the energy barrier, \( T \) is temperature, \( k \) is Boltzmann's constant and \( n_0 \) the prefactor. The prefactor can be determined using the Vineyard method [14]. If we use a typical value of \( n_0 = 10^{12} \text{s}^{-1} \) [16], then we find hop times out of the substitutional site of around 2 min and 16 days for the energy barriers of 1.4 and 1.8 eV respectively at 500 K. The reverse barriers are tiny so even if the atom succeeded in jumping to a nearby interstitial site it would rapidly recombine.

Once the inert gas atoms have become substitutional they create a nearby Fe dumbbell interstitial. Thus it is instructive to examine the energy barriers for the Fe interstitial to diffuse away from the substitutional inert gas atom. It is known from both ab initio [17] and empirical potential calculations [16] that the lowest energy Fe interstitial is the \(<110>\) dumbbell which diffuses with a barrier of 0.3 eV. Fig. 4 shows a similar energy barrier so the dumbbell interstitial is not bound to an Ar substitutional atom and could diffuse away as easily as it could diffuse in the perfect Fe lattice (hop time of \( \approx 1 \text{ ns} \) at 500 K). An almost identical situation exists if the substitutional atom is Xe.

This suggests that in contrast to He, energetic Ar or Xe produced either by a nuclear reaction or inserted into a lattice by ion implantation would not diffuse and accumulate into bubbles at low temperature but instead after losing kinetic energy through

![Graph of frequency vs additional vacancies](image)

**Fig. 7.** Frequency of capture/loss of vacancies after collision cascades near a bubble containing 15 vacancies. The three results show cases of (1) below the ideal gas-vacancy ratio, (2) at the optimal and (3) above the ideal ratio.
ballistic collisions would quickly occupy nearby substitutional sites. The displacement of a lattice atom by the inert gas has sometimes been referred to as trap mutation in the previous literature and is well known for the case of He in W [15]. The Fe interstitial could then easily diffuse away to find other sink sites, such as a nearby grain boundary.

The question therefore arises as to whether bubbles of Ar and Xe can actually form in the material during these processes. Are there other diffusion mechanisms that could give rise to bubble formation and if a bubble actually forms, by what mechanism could it grow?

4.1. Vacancy driven diffusion mechanisms

Another possibility for a substitutional Ar or Xe atom to diffuse in the lattice is through a vacancy-driven mechanism. We therefore examine the diffusion barriers for substitutional atoms in the presence of 1–2 vacancies.

Fig. 5a,b shows that the energy barriers for a nearby vacancy to diffuse towards the Ar substitutional atom are lower than in the bulk crystal (0.64 eV, [16]). Thus vacancies are attracted to substitutional Ar. For a single vacancy, the lowest energy structure for both Ar and Xe is the <111> split vacancy complex. This can diffuse as a unit but the lowest energy barriers are 1.9 eV and 2.0 eV for Ar and Xe respectively as illustrated in Fig. 5f for Ar. The identical mechanism exists in the case of Xe. A well-known vacancy assisted mechanism for diffusion is the so-called five frequency model [18]. However Fig. 5e shows that this mechanism is not preferred here since the reverse barrier for a split vacancy structure to return to a substitutional gas atom and a fourth neighbour vacancy is 2.65 eV which is much higher than if the complex diffuses as a whole. Other diffusion mechanisms are also shown in the figure. These mechanisms and the values of the energy barriers were calculated using the dimer and RAT methods from several hundred searches and checked using the NEB method. Since these methods make no assumption about the final state we are confident that the lowest energy diffusion mechanisms were obtained.

If the initial structure is composed of a substitutional inert gas atom with 2 adjacent vacancies, the complex evolves to an isosceles triangle structure with the inert gas atoms located at the centroid. This structure can diffuse as a unit with similar energy barriers to the split vacancy complex, 1.8 eV and 2.1 eV for Ar and Xe respectively. See Fig. 6. Since these energy barriers are high it seems unlikely that inert gas atoms could diffuse through the system through a vacancy driven mechanism to create bubbles unless the temperature is very high.

4.2. Pre-existing inert gas bubbles

It is instructive to examine the effect of irradiation on any pre-existing Ar or Xe bubbles in the material since it was previously shown in the case of He bubbles that they could be enlarged by irradiation through the capture of vacancies (emission of Fe interstitials). Following the same procedure as in the case of He [3] we initiated 8000 separate cascades by imparting 1 keV of energy to nearby Fe atoms in the lattice and examined the resulting bubbles after the irradiation events. The statistics are presented in Fig. 7a and b for bubbles that initially contained 15 vacancies. It can be seen, as was the case with He bubbles, that the bubbles can enlarge by vacancy capture. Because of the lattice strain around the bubble it is easier for any emitted Fe interstitial atoms to diffuse away from the bubble than to return. Fe interstitial return to the bubble was not observed during the time scale of the MD simulations (10ps). It is only in the case where the bubbles contain fewer inert gas atoms than those corresponding to the minima on the curves in Figs. 1 and 3 that Fe interstitials produced by irradiation reduce a bubble’s size. Irradiation might therefore provide a mechanism for an existing bubble to be enlarged by allowing nearby inert gas atoms to join. Thus the effect of a bubble on nearby substitutional Ar and Xe atoms was examined. It was not possible to calculate energy barriers for substitutional atoms located in positions up to 0.5 nm from the edge of an existing bubble since such atoms joined the bubble during energy system minimisation, both using conjugate gradient and damped MD, thus indicating that a capture zone exists. The energy barriers for substitutional atoms located at distance greater than ≈ 0.55 nm to join the bubble are slightly reduced from the bulk values but still exceed 1.7 eV. Thus a possible mechanism for bubble enlargement is vacancy capture together with movement of inert gas atoms induced by irradiation into the capture zone.

5. Conclusion

Ar and Xe bubbles in a bcc Fe crystal lattice have been examined and the optimal gas to vacancy ratio determined. Unlike the case of He, the larger sized Ar and Xe atoms cannot easily diffuse through the crystal as they prefer to locate at substitutional sites. This suggests that bubble formation and the resulting loss of structural integrity, may be much less of a problem compared to the case of He. Bubbles could form and enlarge through irradiation induced mechanisms but this would entail much larger doses than in the case of He.

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