First-principles study of diffusion behaviors of Cs and I in Cr coating

Authors: Shuying Lin, Xiaojing Li, Linbing Jiang, Xijun Wu, Huiqin Yin, Yu Ma, Wenguan Liu, Yu Ma, Liu Wenguan

Date: 2024-03-13T00:00:00+00:00

Abstract

Cs and I can migrate through the fuel-cladding interface and accelerate the cladding corrosion process induced by the Fuel Cladding Chemical Interaction. Cr coating is an important candidate in mitigating this chemical interaction. First-principles calculations were employed to investigate the diffusion behaviors of Cs and I in Cr bulk and Cr grain boundary, aiming to reveal the microscopic mechanisms for mitigating the interaction at fuel-cladding interface. The interactions between these two fission products and Cr coating were systematically studied, and the temperature-dependent diffusion coeffcients of Cs and I in Cr were obtained using Bocquet' s oversized solute atoms model and Le Claire' s nine-frequency model, respectively. The results show that the migration barriers of Cs and I are significantly lower compared to that of Cr, and the diffusion coeffcients of Cs and I are both more than 3 orders of magnitude larger than Cr self-diffusion coeffcient within the temperature range of Generation IV fast reactors (below 1000 K), which shows the strong penetration ability of Cs and I. Meanwhile, Cs and I are more likely to diffuse along the grain boundary because of the generally low migration barriers, indicating that grain boundary serves as a fast diffusion channel for Cs and I.

Full Text

Preamble

First-Principles Study of Diffusion Behaviors of Cs and I in Cr Coating

Shuying Lin,[1] Xiaojing Li,[1] Linbing Jiang,[1] Xijun Wu,[2] Huiqin Yin,[1] Yu Ma,[1],† and Wenguan Liu[1],‡
[1]Sino-French Institute of Nuclear Engineering and Technology, Sun Yat-Sen University, Zhuhai, 519082, China

[2]School of Nuclear Science and Technology, University of South China, Hengyang, 421001, China

Cesium and iodine can migrate through the fuel-cladding interface and accelerate the cladding corrosion process induced by Fuel Cladding Chemical Interaction (FCCI). Chromium coating represents an important candidate for mitigating this chemical interaction. First-principles calculations were employed to investigate the diffusion behaviors of Cs and I in Cr bulk and at Cr grain boundaries, aiming to reveal the microscopic mechanisms for mitigating the interaction at the fuel-cladding interface. The interactions between these two fission products and Cr coating were systematically studied, and the temperature-dependent diffusion coefficients of Cs and I in Cr were obtained using Bocquet' s oversized solute atoms model and Le Claire' s nine-frequency model, respectively. The results show that the migration barriers of Cs and I are significantly lower compared to that of Cr, and the diffusion coefficients of Cs and I are both more than three orders of magnitude larger than the Cr self-diffusion coefficient within the temperature range of Generation IV fast reactors (below 1000 K), demonstrating the strong penetration ability of Cs and I. Meanwhile, Cs and I are more likely to diffuse along the grain boundary because of the generally low migration barriers, indicating that the grain boundary serves as a fast diffusion channel for Cs and I.

Keywords: First-principles calculation, Fuel Cladding Chemical Interaction, Cr coating, Fission product, Diffusion, Grain boundary

Introduction

Fuel Cladding Chemical Interaction (FCCI) is considered one of the major factors limiting the lifetime of fuel pins in fast reactors, especially for oxide fuel pins with stainless steel cladding [1], as severe oxidative corrosion can occur at the interface between the fuel and the inner wall of the cladding. Some fission products, migrating through the fuel-cladding interface, can accelerate the FCCI-induced cladding corrosion process, with the main fission products involved being volatile Cs and I [1, 2] considering their production yield and penetrating depth.

Since the cladding attack rate depends on the diffusion of reactants at the cladding surface, the diffusion of Cs and I in fuel pins represents a key factor in FCCI-induced corrosion problems. Due to the complex and multiscale coupled physical and chemical mechanisms of FCCI, current research mainly focuses on exploring materials that can mitigate FCCI through experimental studies, and a coating of buffer-getter materials on the cladding inner surface is considered an effective method [1]. Buffer-getter materials including V, Nb, Cr, Zr, U, Ti, and certain rare earth metals can reduce oxidation of the cladding due to their high affinity for oxygen [1]. Specifically, Cr coating features a high melting point, superior oxidative corrosion resistance [3, 4], good crack resistance [5–7], and mature preparation processes [8–10], making it an important candidate for

mitigating FCCI, though the underlying micro-mechanisms remain unknown.

First-principles density functional theory (DFT) is recognized as a powerful tool for revealing micro-mechanisms, especially from the perspective of elemental diffusion behaviors when coupled with harmonic transition state theory [11], as demonstrated by numerous previous works on impurity diffusion and its consequent effects in Ni [11–16], Fe [17–24], Al [25–27], SiC [28], etc. Recently, Yang et al. have carried out first-principles calculations of lanthanide diffusion in Cr and α-Fe to identify FCCI-mitigating mechanisms for metallic fuel and ferritic/martensitic steel cladding systems [22]. To our knowledge, there remain few investigations of FCCI-involved elements for oxide fuels, in which Cs and I dominate. Furthermore, additional investigation is warranted to comprehensively understand how Cr coating functions on the cladding inner surface to mitigate FCCI for oxide fuel pin systems.

In this work, first-principles methods were employed to investigate the diffusion behaviors of important fission products (Cs and I) in BCC Cr coating. Cs and I are so large in the Cr matrix that diffusion via interstitial atoms [29–33] was deemed unrealistic. Instead, vacancy-mediated diffusion represents the main mode of diffusion for impurity atoms of large atomic size [34], such as Cs and I. Section 2 lays out the vacancy-mediated diffusion models and details of the first-principles calculations, and the methodology for determining the inputs for diffusion models is also presented. Section 3 discusses the interactions between impurity atoms and the surrounding Cr atoms or vacancies. Diffusion coefficients of Cs and I in BCC Cr were obtained by applying the diffusion model, and possible diffusion paths of Cs and I at grain boundaries (GB) were predicted based on results of migration barriers between different sites.

[Figure 1: see original paper]

II. Computational Methods

A. Diffusion Models for Vacancy-Mediated Solutes

In this section, two diffusion models for determination of impurity diffusion coefficients are introduced: Le Claire' s nine-frequency model [35–37] (referred to as Le Claire' s model) and the oversized solute-atom (OSA) model [21]. As shown in Fig. 1, impurity atoms and matrix atoms are represented by orange and blue spheres, respectively, and vacancies by gray squares. The numbers on the atoms and vacancies indicate their positions as the nearest neighbors (nn) to the impurity atom, and the corresponding jump frequencies for different atom-vacancy exchange processes are also labeled in Fig. 1. The main difference between the two diffusion models lies in the configuration formed by the impurity atom and its 1nn vacancy, which will be described in detail below.

According to Le Claire' s model [35–37], the self-diffusion coefficient ($D_{\text{self-diff}}$) and the solute diffusion coefficient (D_{solute}) in BCC lattice can be obtained by:

$$D_{\text{self-diff}} = a^2 \omega_0 f_0 C_V$$

$$D_{\text{solute}} = a^2 \omega_2 f_x C_V \exp\left(\frac{E_b^1}{k_B T}\right)$$

with a the lattice parameter, E_b^1 the vacancy-solute binding energy when the vacancy is located on the 1nn site of the solute, k_B the Boltzmann constant, and T the temperature in K. f_0 is the correlation factor for self-diffusion, which is a constant equal to 0.727 for diffusion in BCC crystals. The correlation factor for solute diffusion f_x can be expressed as [35–37]:

$$f_x = \frac{3\omega_3 + 3\omega_3' + \omega_3'' - 2\omega_2 F\omega_5}{3\omega_3 + 3\omega_3' + \omega_3'' + \omega_4 + F\omega_5} \times \frac{2\omega_3'\omega_4'\omega_4' + 3F\omega_0}{2\omega_3'\omega_4'\omega_4' + 3F\omega_0 + \omega_3''\omega_4''\omega_4'' + 7F\omega_0}$$

where $F = 0.512$. This expression applies to the case where the impurity atom is close in size to the matrix atom, with the approximation $\omega_6 = \omega_0$. Based on transition-state theory [35], the average atomic jump frequency ω_i can be written with respect to the migration energy (E_m^i) as:

$$\omega_i = \nu_i \exp\left(-\frac{E_m^i}{k_B T}\right)$$

in which ν_i and E_m^i are the attempt frequency and corresponding migration barrier for jump i, respectively. ν_i is defined as $\nu_i = \frac{\prod_{j=1}^{3N-4} \nu_j^I}{\prod_{j=1}^{3N-3} \nu_j^T}$, in which ν_j^I are the normal vibration frequencies of the initial state (I) of migration, and ν_j^T are the non-imaginary normal frequencies of the transition state (T). The vacancy concentration at equilibrium at temperature T is given by $C_V = \exp\left(-\frac{E_f^v}{k_B T}\right) \exp\left(\frac{S_f^v}{k_B}\right)$, with the vacancy formation energy $E_f^v = E_I - (N-1)E_B/N$ and the vacancy formation entropy $S_f^v = k_B \left[\ln\left(\frac{\prod_{j=1}^{3N-3} \nu_j^I}{\prod_{j=1}^{3N} \nu_j^B}\right) - \frac{N-1}{N} \ln\left(\frac{\prod_{j=1}^{3N-3} \nu_j^B}{\prod_{j=1}^{3N} \nu_j^B}\right)\right]$, in which E_I and E_B are the corresponding energies of the initial state structure and the bulk structure containing $N-1$ and N atoms, respectively, and ν_j^B are the normal vibration frequencies of the bulk structure (B).

Le Claire' s model is the commonly used diffusion model which describes well the diffusion of substitutional solutes. Nevertheless, due to the strong attraction of the OSA to the vacancy (as illustrated in Fig. 1(b)), the diffusion of OSA cannot be described by Le Claire' s model. Bocquet et al. proposed a diffusion model applicable to OSA, i.e., the OSA model, and the expression for the OSA diffusion coefficient is given by [21]:

$$D_{\mathrm{OSA}} = \Gamma_{MJ}\lambda^2 f$$

where λ is the distance between the vacancy and its nearest atom, i.e., $\lambda = \sqrt{3}a/2$ in BCC crystals, Γ_{MJ} is the frequency attached to a macrojump (MJ), and f is the correlation factor. A macrojump is formed by two elementary displacements: the OSA located on a substitutional site (S) is pushed onto a transitional site (T), i.e., $S \to T$, and then moves onto an S site from the T site ($T \to S$). In this way, the frequency attached to a MJ is defined as:

$$\Gamma_{MJ} = \frac{\Gamma_{ST}\Gamma_{TS}}{\Gamma_{ST} + \Gamma_{TS}}$$

with

$$\Gamma_{ST} = 8C_V \left[3\omega_4 \exp\left(\frac{E_b^1}{k_B T}\right) + 3\omega_4' \exp\left(\frac{E_b^2}{k_B T}\right) + \omega_4'' \exp\left(\frac{E_b^3}{k_B T}\right)\right]$$

and

$$\Gamma_{TS} = 2 \times (3\omega_3 + 3\omega_3' + \omega_3'')$$

E_b^i is the binding energy between the solute and its ith nn vacancy (positive value for attraction, and vice versa), and can be calculated by:

$$E_b^i = E_V + E_S - E_I - E_B$$

The terms on the right side of the equation represent the energies of different configurations, and the numbers of Cr atoms, vacancies, and impurity atoms in each configuration are (127, 1, 0), (127, 0, 1), (126, 1, 1), and (128, 0, 0), respectively. The correlation factor f for OSA diffusing in BCC crystals equals to $1+Q_{\mathrm{BCC}}$, in which Q_{BCC} is the average cosine between a $T \to S$ jump vector and the next $S \to T$ jump in the BCC lattice. Bocquet et al. obtained the exact formula of Q_{BCC} by a double Laplace and Fourier transform of the transport equation for the vacancy. For simplification, we applied the formula with the "one-shot" approximation [21]:

$$Q_{\mathrm{BCC}}^{\mathrm{1shot}} = -\frac{3\omega_3 + 3\omega_3' + \omega_3''}{4\omega_3\omega_4 + 4\omega_5} \times \frac{4\omega_3'\omega_4'}{2\omega_4' + 6\omega_0} \times \frac{\omega_3''\omega_4''}{\omega_4'' + 7F\omega_0}$$

The hypothesis of the "one-shot" approximation is that, after the dissociation of the OSA and its nearby vacancy, only one jump is needed for the vacancy to

return close to the OSA. This approximation is proven valid when the vacancy-solute interaction is very strong at 1nn, which is exactly the case for OSA diffusion.

Our preliminary calculations show that Cs combines with its 1nn vacancy and forms a "V/2 + Cs + V/2" configuration (V for vacancy), corresponding to Fig. 1(b). In contrast, I does not exhibit strong attraction to the 1nn vacancy, corresponding to Fig. 1(a). According to the applicable conditions for different diffusion models, the OSA model is used for calculating Cs diffusion coefficients, while the Le Claire model is used for I in this study.

B. First-Principles Calculations

To investigate the diffusion behaviors of Cs and I in BCC Cr coating, density functional theory (DFT) calculations were performed with the Vienna ab initio simulation package (VASP) [39–41] using projector augmented wave (PAW) [42] pseudopotentials and Perdew-Burke-Ernzerhof (PBE) [43] parametrization. Razumovskiy et al. found that disordered local-moment calculations for pure Cr in the paramagnetic state reduce to a nonmagnetic solution [44]. A $4 \times 4 \times 4$ supercell containing 128 atoms was adopted for simulation of the Cr matrix, and the $\Sigma5(210)$ GB supercell consisting of 76 sites was used for simulation at the Cr GB, as shown in Fig. 2.

The Brillouin zone was sampled with $4 \times 4 \times 4$ and $5 \times 5 \times 1$ k-point meshes for the Cr matrix and GB, respectively. The total energy and force convergence criteria were set to 1.0×10^{-5} eV and 0.01 eV/Å, respectively, with a cutoff energy of 400 eV. All transition states and migration barriers were obtained by applying the climbing image Nudged Elastic Band (cNEB) method, using three intermediate images. To determine the diffusion coefficients in the Cr matrix, phonon calculations were also performed considering only the vibrational modes of the migrating atoms [22, 45–48]. For both the search of transition states and phonon calculations, the force convergence criterion was reset to 0.001 eV/Å, as the results are highly sensitive to this parameter.

[Figure 2: see original paper]

III. Results and Discussion

Impurity Diffusion in Cr Matrix

1. Atomic Structure and Electron Distribution in Matrix The interaction between atoms can change the forces acting on the impurity, thus representing an important factor affecting migration behaviors. Fig. 3 illustrates the change in bond lengths caused by a substitutional impurity. Both Cs and I exert a repulsive effect on the surrounding Cr atoms because the Bader radii of Cs and I shown in Table 1 are both larger than that of Cr. The effect of Cs is more significant, with the bond lengths of its 1nn and 2nn increasing by more than 0.1 Å.

To better understand the effect of impurities, the electronic structure with impurities was further analyzed. Using the Bader decomposition method [49], Bader charge, volume, and radius [50] were calculated and listed in Table 1. For the Cr atoms, the Bader charge and atomic volume of the 127 Cr atoms are almost identical, so their average values are given directly in the table. Both Cs and I gain electrons from the matrix, with the non-metallic I atom gaining reasonably more electrons than the metallic Cs atom. The atomic volumes of Cs and I are almost the same.

The binding effect between impurity atoms and their surrounding Cr atoms is weaker compared to that between Cr atoms, which can be observed from the charge densities between the impurity atoms and their 1nn Cr atoms shown in Fig. 4. The charge density around the impurity atoms decreases significantly compared to the corresponding profile for the pure Cr system (Fig. 4(a)), which is consistent with the effect of increasing bond length shown in Fig. 3. Additionally, the presence of impurity atoms increases the charge density between Cr atoms in the diagonal direction, indicating enhanced interaction between them. Taken together, Cr atoms near the impurity atoms tend to move away from the impurity atoms and have weak binding interactions with them, favoring the diffusion of impurity atoms in the matrix.

The binding effect of Cr atoms to Cs is slightly weaker than that to I. Comparing the results for Cs and I (Fig. 4(b) & (c)), the charge density distributions are similar, but in terms of equipotential lines, the charge density around Cs is more dilute and the interaction with Cr atoms is weaker than that of I. This is also consistent with the fact that the Cs-Cr bonds are longer than the I-Cr bonds in Fig. 3 and can be observed in Fig. 5. There is no hybridization peak between Cs and Cr atoms, indicating metallic bonds, while several hybridization peaks appear between I and Cr atoms, indicating covalent-like bonds. Specifically, the d electrons of Cr and the p electrons of I are mainly involved in hybridization between -9 and -3 eV, and the d electrons of Cr and I are mainly involved in hybridization between -2 and 0 eV. Overall, Cs and I have similar effects on the Cr matrix, with slightly lower interactions around Cs than I.

[Figure 3: see original paper]

The attempt frequencies of vacancies moving away from the impurity atoms (ν_3, ν_3', ν_5) are also generally lower than the attempt frequencies near the impurity atoms (ν_4, ν_4', ν_6). This indicates that vacancies are more likely to be attracted to and remain near the impurity atoms, which is also consistent with the results shown in Fig. 6. This attractive effect on vacancies facilitates the diffusion of impurity atoms.

2. Diffusion Process and Diffusion Coefficient in Matrix To investigate the effect of impurity atoms on neighboring vacancies, the binding energies of impurity atoms to neighboring vacancies were calculated according to Eq. (6) and the results from 1nn to 4nn are shown in Fig. 6. The binding en-

ergy involving the 5nn vacancy is not presented because the 5nn vacancy slides spontaneously into the 1nn position (i.e., the Cr atom in the 1nn position of the impurity slides spontaneously into the 5nn position). Both impurity atoms have an attractive effect on vacancies from 1nn to 4nn. The binding energy of Cs to the 1nn vacancy is up to 2.46 eV, which is a possible reason for the formation of the "V/2 + Cs + V/2" configuration. The relatively low binding energy between I and its 1nn vacancy may be the reason why I remains stable at the substitutional site. The binding energies of Cs to vacancies are generally higher than those of I, especially for the 1nn and 2nn vacancies. However, for the 3nn and 4nn vacancies, the binding energies are almost the same, indicating that impurity atoms mainly affect the 1nn and 2nn vacancies.

Migration energy and the attempt frequency required for vacancies near the impurity to move onto different sites are also important factors affecting the difficulty of migration processes. The results in Table 2 indicate that impurity atoms are favored in the competition for vacancies with the surrounding matrix atoms. The migration barriers of vacancies moving away from the impurity atoms (E_m^5) are generally higher than those in the direction close to the impurity atoms (E_m^6), and the energy required for vacancies located at the 3nn of the impurity atoms to migrate to the 1nn is lower than that required for self-diffusion in the pure Cr system (0.92 eV shown in Fig. 7). In terms of attempt frequencies, the attempt frequencies of vacancies moving away from the impurity atoms (ν_3, ν_3', ν_5) are also generally lower than the attempt frequencies near the impurity atoms (ν_4, ν_4', ν_6). This indicates that vacancies are more likely to be attracted to and remain near the impurity atoms, which is also consistent with the results shown in Fig. 6. This attractive effect on vacancies facilitates the diffusion of impurity atoms.

Both Cs and I can diffuse easily in the Cr matrix because of their low migration barriers. As illustrated in Fig. 7(a) & (b), Cs will spontaneously move from the substitutional site to the middle point of the two lattice sites, while I must overcome a migration barrier of 0.36 eV to move to another substitutional site. Although the migration of I is not spontaneous, the migration barrier is lower than that for Cr atoms (0.92 eV according to our calculations). As a result, the diffusion of both Cs and I is easier than Cr self-diffusion. Nevertheless, the migration barrier results do not necessarily imply that Cs diffusion is faster than I, as the displacement that occurs by diffusion for Cs is $3a/2$, which is twice that of I.

Before determining the diffusion coefficients of Cs and I in Cr, approximations must be made for the phenomenon of spontaneous sliding of the 5nn vacancy of the impurity to the 1nn position. Since this process proceeds spontaneously, it is not possible to find the corresponding vacancy jump frequency according to Eq. (4). According to the assumptions of the Le Claire and OSA models, the frequency of exchange of the 5nn vacancy with the atom further away from the impurity is considered to be the jump frequency of Cr atom self-diffusion. In our DFT simulations, the 5nn vacancy will only slide into the 1nn position, so

we can define: $\omega_4'' = \omega_0$, $\omega_3'' = 0$.

Based on all the assumptions made, the diffusion coefficients of Cs and I in the Cr matrix at 500–2000 K can be calculated according to the OSA model and Le Claire model, respectively, as shown in Fig. 8. The results of Cr self-diffusion coefficients are shown for comparison, which are in good agreement with experimental data [51, 52]. It can be seen that the diffusion coefficients of the impurity atoms are larger than the self-diffusion coefficients of Cr in the temperature interval considered. This can be attributed to the combined effect of three factors analyzed in preceding paragraphs: weaker bonding effect by the surrounding Cr atoms, stronger attraction effect for nearby vacancies, and lower migration barriers compared to the Cr self-diffusion process. In the temperature range of Generation IV fast reactors (around 500–1000 K), the diffusion coefficients of Cs and I are 3–7 orders of magnitude larger than the self-diffusion coefficients of Cr, which also indicates the strong penetration ability of Cs and I. The diffusion coefficients of all three elements increase exponentially with increasing temperature. Despite the different diffusion characteristics of Cs and I shown in Fig. 7, the diffusion coefficients of Cs and I are very close in the temperature range considered. Because our calculations of Cr self-diffusion coefficients agree well with experimental results, the diffusion coefficients of Cs and I in BCC Cr from DFT calculations are reliable.

The self-diffusion coefficient of BCC Cr, D_{Cr} (cm^2/s), can be recalculated using the following equation based on parameters obtained in this study:

$$D_{\mathrm{Cr}} = 0.1323 \times \exp\left(-\frac{4.0861 \times 10^4}{T}\right)$$

and the diffusion coefficients of Cs and I in BCC Cr, D_{Cs} and D_{I} (cm^2/s), can be fitted from Fig. 8 as:

$$D_{\mathrm{Cs}} = \exp\left[(-5.8676 \pm 0.0051) - \frac{(2.6915 \pm 0.0004) \times 10^4}{T}\right]$$

$$D_{\mathrm{I}} = \exp\left[(-1.8582 \pm 0.0158) - \frac{(3.4297 \pm 0.0016) \times 10^4}{T}\right]$$

[Figure 7: see original paper]

[Figure 8: see original paper]

Impurity Diffusion at Cr GB

1. Atomic Structure and Electron Distribution at the GB The grain boundary serves as a fast diffusion channel for impurity atoms, and the presence of Cs and I atoms on the GB plane changes the GB structures, such as bond

lengths and charge distributions. In this subsection, the impurity atom was placed at site 1 on the GB plane to analyze these changes and the differences between the matrix and GB. As shown in Fig. 9, the presence of impurity atoms at the GB does not lead to an increase in all bond lengths, which differs from the behavior in the matrix. Nevertheless, impurity atoms located at this substitution site significantly increase the bond length in the [210] direction, i.e., distancing the atoms on both sides of the GB plane. This facilitates the diffusion of impurity atoms along the interface. Additionally, Cs has a more pronounced effect on increasing this bond length than I, which is consistent with the results in Fig. 3.

The Bader charge, volume, and radius [50] of atoms at the GB were obtained using the Bader decomposition method [49] as in the matrix, and the results are demonstrated in Table 3. As in the matrix, the Bader results for the 75 Cr atoms at the GB were found to be similar, so their average values were used for analysis. Comparing Table 1 with Table 3 reveals that the I atom gains electrons both in the matrix and at the GB, while the Cs atom loses electrons at the GB, which differs from the case in the matrix. For I substitution, the number of electrons gained at the GB is slightly less compared to that in the matrix, probably because the atomic structure at the GB is not as compact as in the matrix and electrons are transferred less between different nuclei. The atomic volumes of Cs and I at the Cr GB are essentially the same as in the Cr matrix. The difference is that the Bader volume of all atoms at the GB is slightly larger than that in the matrix, which is reasonable because the atomic arrangement at the GB is sparser. This is also favorable for the migration of Cs and I atoms, and it can be expected that impurity atoms on the GB plane will migrate more easily than in the matrix.

Both Cs and I have similar effects at the Cr GB as in the matrix, with slightly lower interactions around Cs than I, as shown in the charge density distributions in Fig. 10. The charge density around the impurity atoms is significantly lower compared to that at the pure Cr GB, which is similar to the behavior in the Cr matrix (Fig. 4). The dilute charge density indicates weak interaction between the impurity atoms and their surrounding Cr atoms, which favors the migration of impurity atoms along the GB plane. Comparing the charge distributions in Fig. 10(b) & (c), the charge density around Cs is smaller than that around I, i.e., the Cs-Cr binding is weaker than the I-Cr binding, which also agrees with the change in bond length in the [210] direction shown in Fig. 9. Compared to the charge density distribution in the matrix (Fig. 4), the charge density distribution at the GB is more dilute. As a result, it can be predicted that the diffusion rates of Cs and I at the GB should be comparable, and the diffusion should be much easier than in the matrix.

[Figure 9: see original paper]

[Figure 10: see original paper]

2. Diffusion Barrier and Diffusion Path Along the GB To investigate impurity diffusion behaviors along the GB, impurity atoms were placed at interstitial site 0 and substitutional sites 1 and 2 on the GB plane (as shown in Fig. 2(b)) as initial structures for different migration processes, and the results of optimization of these initial structures are shown in Table 4. It can be observed that impurity atoms located at site 0 will spontaneously migrate to the non-occupied site 2, which is more stable than site 0. If a vacancy is introduced at site 1, the impurity atoms located at site 2 will spontaneously migrate to site 1, which is more stable than site 2. Both of these migration processes occur spontaneously, so the impurity atoms can readily diffuse along the GB direction.

The calculated migration barriers between site 0 and site 1 are shown in Fig. 11. The migration barriers from site 0 to site 1 for Cs and I are obviously smaller compared to those in the matrix (Table 2), indicating that GBs are fast channels for impurity diffusion in Cr. Nevertheless, Cs or I needs to overcome a high energy barrier (up to 4.90 eV or 3.53 eV) to migrate from site 1 to site 0, meaning that impurity diffusion is directional in some GB regions.

In summary, two additional possible paths were predicted for the diffusion of impurity atoms along the GB plane, as shown in Fig. 12 & 13. Both migration paths require the introduction of vacancies at the GB plane, and many vacancies exist in the GB region of real materials. Furthermore, the vacancy concentration can be significantly increased by the combined effect of high temperature and irradiation under service conditions on the inner surface of the cladding in nuclear reactors. In Fig. 12, vacancies at sites 2 and 1 were introduced in succession, and the impurity atoms at site 0 move spontaneously, sliding sequentially to site 2 and then to site 1. In Fig. 13, one vacancy was introduced at site 1, and due to the low migration barrier from sites 0 to 1, the impurity atoms can easily move to site 1.

[Figure 11: see original paper]

[Figure 12: see original paper]

[Figure 13: see original paper]

IV. Summary

The diffusion behaviors of Cs and I, key elements of FCCI, in Cr coating were investigated using DFT approaches together with Le Claire and OSA diffusion models. Under the combined effect of low binding with matrix atoms and strong binding with nearby vacancies, the migration barriers of Cs and I are both lower compared to that of Cr. As a result, the diffusion coefficients of Cs and I are both 3–7 orders of magnitude larger than the Cr self-diffusion coefficient below 1000 K, which corresponds to the temperature range of Generation IV fast reactors. Despite the differences in migration barriers and displacements of the elemental diffusion processes of Cs and I, and also the different models used, the diffusion coefficients obtained for Cs and I are basically the same order of magnitude at

the temperatures considered. Meanwhile, the results for Cr self-diffusion agree well with experimental values, by which our results can be considered accurate. Based on our results, the diffusion paths of Cs and I in the inner-surface Cr coating of the cladding were predicted. Cs and I are more likely to diffuse along the GB, and intergranular corrosion still requires further investigation.

V. Appendix

List of Abbreviations

Abbreviation	Definition
BCC	Body Centered Cubic
cNEB	climbing image Nudged Elastic Band
DFT	Density Functional Theory
FCCI	Fuel Cladding Chemical Interaction
GB	Grain Boundary
nn	nearest neighbors
OSA	Oversized Solute-Atom
PAW	Projector Augmented Wave
PBE	Perdew-Burke-Ernzerhof
VASP	Vienna ab initio simulation package

[1] K. Maeda, 3.16 - Ceramic Fuel–Cladding Interaction, in: R.J.M. Konings (Ed.) *Comprehensive Nuclear Materials*, Elsevier, Oxford, 2012, pp. 443-483.
[2] R. Parrish, A. Aitkaliyeva, A review of microstructural features in fast reactor mixed oxide fuels. *J. Nucl. Mater.* 510, 644-660 (2018). doi:10.1016/j.jnucmat.2018.05.076
[3] W. Zhong, P.A. Mouche, B.J. Heuser, Response of Cr and Cr-Al coatings on Zircaloy-2 to high temperature steam. *J. Nucl. Mater.* 498, 137-148 (2018). doi:10.1016/j.jnucmat.2017.10.021
[4] J.-C. Brachet, I. Idarraga-Trujillo, M.L. Flem et al., Early studies on Cr-Coated Zircaloy-4 as enhanced accident tolerant nuclear fuel claddings for light water reactors. *J. Nucl. Mater.* 517, 268-285 (2019). doi:10.1016/j.jnucmat.2019.02.018
[5] J. Jiang, H. Zhai, P. Gong et al., In-situ study on the tensile behavior of Cr-coated zircaloy for accident tolerant fuel claddings. *Surf. Coat. Technol.* 394, 125747 (2020). doi:10.1016/j.surfcoat.2020.125747
[6] J. Jiang, D. Zhan, J. Lv et al., Comparative study on the tensile cracking behavior of CrN and Cr coatings for accident-tolerant fuel claddings. *Surf. Coat. Technol.* 409, 126812 (2021). doi:10.1016/j.surfcoat.2020.126812
[7] J.-S. Jiang, D.-Q. Wang, M.-Y. Du et al., Interdiffusion behavior between Cr and Zr and its effect on the microcracking behavior in the Cr-coated Zr-4 alloy. *Nucl. Sci. Tech.* 32, 134 (2021). doi:10.1007/s41365-021-00977-w
[8] J. Bischoff, C. Delafoy, N. Chaari et al., Cr-coated cladding development at Framatome, Topfuel 2018-Light Water Reactor (LWR) Fuel Performance

Meeting 2018.
[9] J. Bischoff, C. Delafoy, C. Vauglin et al., AREVA NP' s enhanced accident-tolerant fuel developments: Focus on Cr-coated M5 cladding. *Nucl. Eng. Technol.* 50, 223-228 (2018). doi:10.1016/j.net.2017.12.004
[10] J. Yang, M. Steinbrück, C. Tang et al., Review on chromium coated zirconium alloy accident tolerant fuel cladding. *J. Alloys Compd.* 895, 162450 (2022). doi:10.1016/j.jallcom.2021.162450
[11] H. Wu, T. Mayeshiba, D. Morgan, High-throughput ab-initio dilute solute diffusion database. *Sci. Data* 3, (2016). doi:10.1038/sdata.2016.54
[12] C.E. Campbell, W.J. Boettinger, U.R. Kattner, Development of a diffusion mobility database for Ni-base superalloys. *Acta Mater.* 50, 775-792 (2002). doi:10.1016/S1359-6454(01)00383-4
[13] A. Janotti, M. Krčmar, C. Fu et al., Solute diffusion in metals: larger atoms can move faster. *Phys. Rev. Lett.* 92, 085901 (2004). doi:10.1103/PhysRevLett.92.085901
[14] M. Krčmar, C.L. Fu, A. Janotti et al., Diffusion rates of 3d transition metal in nickel by first-principles calculations. *Acta Mater.* 53, 2369-2376 (2005). doi:10.1016/j.actamat.2005.01.044
[15] I. Lomaev, D. Novikov, S. Okatov et al., First-principles study of 4d solute diffusion in nickel. *J. Mater. Sci.* 49, 4038-4044 (2014). doi:10.1007/s10853-014-8119-1
[16] W.-G. Liu, H. Han, C.-L. Ren et al., The effect of Nb additive on Te-induced stress corrosion cracking in Ni alloy: a first-principles calculation. *Nucl. Sci. Tech.* 25, 050603 (2014). doi:10.13538/j.1001-8042/nst.25.050603
[17] S. Huang, D.L. Worthington, M. Asta et al., Calculation of impurity diffusivities in α-Fe using first-principles methods. *Acta Mater.* 58, 1982-1993 (2010). doi:10.1016/j.actamat.2009.11.041
[18] H. Ding, S. Huang, G. Ghosh et al., A computational study of impurity diffusivities for 5d transition metal solutes in α-Fe. *Scr. Mater.* 67, 732-735 (2012). doi:10.1016/j.scriptamat.2012.06.010
[19] L. Messina, M. Nastar, T. Garnier et al., Exact ab initio transport coefficients in bcc Fe-X (X=Cr, Cu, Mn, Ni, P, Si) dilute alloys. *Phys. Rev. B* 90, 104203 (2014). doi:10.1103/PhysRevB.90.104203
[20] L. Messina, M. Nastar, N. Sandberg et al., Systematic electronic-structure investigation of substitutional impurity diffusion and flux coupling in bcc iron. *Phys. Rev. B* 93, 184302 (2016). doi:10.1103/PhysRevB.93.184302
[21] J.-L. Bocquet, C. Barouh, C.-C. Fu, Migration mechanism for oversized solutes in cubic lattices: The case of yttrium in iron. *Phys. Rev. B* 95, (2017). doi:10.1103/PhysRevB.95.214108
[22] C. Yang, J. Tian, H. Guan et al., Significant difference of lanthanide fission products diffusion in Cr and α-Fe: An atomic-level study. *Scr. Mater.* 227, 115304 (2023). doi:10.1016/j.scriptamat.2023.115304
[23] X. Gao, H. Ren, C. Li et al., First-principles calculations of rare earth (Y, La and Ce) diffusivities in bcc Fe. *J. Alloys Compd.* 663, 316-320 (2016). doi:10.1016/j.jallcom.2015.12.129
[24] D. Murali, B.K. Panigrahi, M.C. Valsakumar et al., Diffusion of Y and

Ti/Zr in bcc iron: A first principles study. *J. Nucl. Mater.* 419, 208-212 (2011). doi:10.1016/j.jnucmat.2011.05.018
[25] N. Sandberg, R. Holmestad, First-principles calculations of impurity diffusion activation energies in Al. *Phys. Rev. B* 73, 014108 (2006). doi:10.1103/PhysRevB.73.014108
[26] M. Mantina, S. Shang, Y. Wang et al., First-principles study of impurity diffusion in aluminum. *Phys. Rev. B* 80, 184111 (2009). doi:10.1103/PhysRevB.80.184111
[27] D. Simonovic, M.H. Sluiter, Impurity diffusion activation energies in Al from first principles. *Phys. Rev. B* 79, 054304 (2009). doi:10.1103/PhysRevB.79.054304
[28] J. Hui, B.-L. Zhang, T. Liu et al., Effects of impurity elements on SiC grain boundary stability and corrosion. *Nucl. Sci. Tech.* 32, 125 (2021). doi:10.1007/s41365-021-00940-9
[29] C. Wert, C. Zener, Interstitial Atomic Diffusion Coefficients. *Phys. Rev.* 76, 1169 (1949). doi:10.1103/PhysRev.76.1169
[30] Y. He, Y. Li, C. Chen et al., Diffusion coefficient of hydrogen interstitial atom in α-Fe, γ-Fe and ϵ-Fe crystals by first-principle calculations. *Int. J. Hydrog. Energy* 42, 27438-27445 (2017). doi:10.1016/j.ijhydene.2017.08.212
[31] D. Connétable, M. David, Diffusion of interstitial species (H and O atoms) in fcc systems (Al, Cu, Co, Ni and Pd): Contribution of first and second order transition states. *J. Alloys Compd.* 772, 280-287 (2019). doi:10.1016/j.jallcom.2018.09.042
[32] M. David, A. Prillieux, D. Monceau et al., First-principles study of the insertion and diffusion of interstitial atoms (H, C, N and O) in nickel. *J. Alloys Compd.* 822, 153555 (2020). doi:10.1016/j.jallcom.2019.153555
[33] X. Yan, P. Li, L. Kang et al., First-principles study of electronic and diffusion properties of intrinsic defects in 4H-SiC. *J. Appl. Phys.* 127, 085702 (2020). doi:10.1063/1.5140692
[34] R. Abbaschian, R.E. Reed-Hill, *Physical Metallurgy Principles-SI Version*, Cengage Learning, 2009.
[35] A. Le Claire, Solvent self-diffusion in dilute bcc solid solutions. *Philos. Mag.* 21, 819-832 (1970). doi:10.1080/14786437008238468
[36] M.J. Jones, A.D. Le Claire, Solvent self-diffusion in dilute b.c.c. solid solutions. *Philos. Mag.* 26, 1191-1204 (1972). doi:10.1080/14786437208227373
[37] A. Le Claire, Solute diffusion in dilute alloys. *J. Nucl. Mater.* 69, 70-96 (1978). doi:10.1016/0022-3115(78)90237-4
[38] G.H. Vineyard, Frequency factors and isotope effects in solid state rate processes. *J. Phys. Chem. Solids* 3, 121-127 (1957). doi:10.1016/0022-3697(57)90059-8
[39] G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals. *Phys. Rev. B* 47, 558-561 (1993). doi:10.1103/physrevb.47.558
[40] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comp. Mater. Sci.* 6, 15-50 (1996). doi:10.1016/0927-0256(96)00008-0
[41] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-

energy calculations using a plane-wave basis set. *Phys. Rev. B* 54, 11169 (1996). doi:10.1103/PhysRevB.54.11169
[42] P.E. Blochl, Projector augmented-wave method. *Phys. Rev. B* 50, 17953 (1994). doi:10.1103/PhysRevB.50.17953
[43] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple. *Phys. Rev. Lett.* 77, 3865 (1996). doi:10.1103/PhysRevLett.77.3865
[44] V.I. Razumovskiy, A.V. Ruban, P.A. Korzhavyi, First-principles study of elastic properties of Cr- and Fe-rich Fe-Cr alloys. *Phys. Rev. B* 84, (2011). doi:10.1103/PhysRevB.84.024106
[45] G. Ho, M.T. Ong, K.J. Caspersen et al., Energetics and kinetics of vacancy diffusion and aggregation in shocked aluminium via orbital-free density functional theory. *Phys. Chem. Chem. Phys.* 9, 4951-4966 (2007). doi:10.1039/b705455f
[46] N. Zou, H.-J. Lu, X.-G. Lu, Impurity diffusion coefficients in BCC Nb from first-principles calculations. *J. Alloys Compd.* 803, 684-688 (2019). doi:10.1016/j.jallcom.2019.06.293
[47] X. Tang, G.B. Thompson, Statistical study of vacancy diffusion in TiC and TaC. *Phys. Rev. Mater.* 4, 093602 (2020). doi:10.1103/PhysRevMaterials.4.093602
[48] L. Yang, N. Kaltsoyannis, Diffusion of krypton and xenon in uranium mononitride; a Density Functional Theory Study. *J. Nucl. Mater.* 566, 153803 (2022). doi:10.1016/j.jnucmat.2022.153803
[49] G. Henkelman, A. Arnaldsson, H. Jónsson, A fast and robust algorithm for Bader decomposition of charge density. *Comp. Mater. Sci.* 36, 354-360 (2006). doi:10.1016/j.commatsci.2005.04.010
[50] R.F. Bader, Atoms in molecules. *Acc. Chem. Res.* 18, 9-15 (1985). doi:10.1021/ar00109a003
[51] J.N. Mundy, C.W. Tse, W.D. McFall, Isotope effect in chromium self-diffusion. *Phys. Rev. B* 13, 2349-2357 (1976). doi:10.1103/PhysRevB.13.2349
[52] J.N. Mundy, H.A. Hoff, J. Pelleg et al., Self-diffusion in chromium. *Phys. Rev. B* 24, 658-665 (1981). doi:10.1103/PhysRevB.24.658

Note: Figure translations are in progress. See original paper for figures.