First-principles study of helium doping at Fe-Cr alloy interfaces

Authors: Lian Xiangyu, Lian Xiangyu

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Abstract

As a candidate material for fusion reactors, low-activation ferritic steel (martensitic steel) is primarily composed of Fe and Cr. Under actual operating conditions, helium generated from fusion reactions penetrates into the material, creating microscopic defects that lead to irradiation damage, thereby affecting the material's radiation resistance (helium embrittlement phenomenon) and other physical properties. This study employs first-principles calculations to simulate the interface of Fe-Cr alloy—the primary reactor structural material—by doping He atoms at various substitutional and interstitial sites. After structural optimization, the formation energy of each configuration is calculated to determine the stability of He atoms at different positions within the Fe-Cr interface. Simultaneously, through volume calculations, it is revealed that He occupying Fe octahedral interstitial sites near the interface induces substantial lattice distortion. Based on analysis of the electronic density of states, we infer that this phenomenon results from mutual hybridization interactions among He, Fe, and Cr atoms at specific locations, providing a theoretical foundation for subsequent investigations into microscopic defects and their physicochemical properties in nuclear-grade stainless steel.

Full Text

Preamble

First-Principles Study on Helium Doping at Fe-Cr Alloy Interfaces

LIAN Xiang-Yu[1],[2]
[1] Anhui Nuclear Exploration Technology Central Institute, Wuhu, Anhui 241000, China
[2] Radioactive Resources and Environmental Engineering Research Center of Anhui Provincial Bureau of Geology and Mineral Resources, Wuhu, Anhui 241000, China

Abstract

Low-activation ferritic/martensitic steels, primary candidate materials for fusion reactor structures, are predominantly composed of Fe and Cr. Under actual operating conditions, helium produced by fusion reactions penetrates the material, generating microscopic defects that cause radiation damage and degrade irradiation resistance (helium embrittlement) as well as other physical properties. This study employs first-principles calculations to simulate helium doping at various substitutional and interstitial sites within Fe-Cr alloy interfaces. By calculating formation energies for each optimized configuration, we determine the relative stability of helium atoms at different interfacial positions. Additionally, volume calculations reveal that helium occupying Fe octahedral interstitial sites near the interface induces significant lattice distortion. Analysis of the electronic density of states suggests this phenomenon results from hybridization among He, Fe, and Cr atoms at specific positions, providing theoretical foundations for investigating microscopic defects and physicochemical properties in nuclear-grade stainless steels.

Keywords: Fe-Cr alloy; first-principles; helium; interface

According to China's *Green Energy Development Outline (2023-2033)* and the *14th Five-Year Energy Plan*, nuclear energy is becoming an increasingly important green energy source that requires active and orderly development. However, the irradiation resistance of reactor materials to hydrogen and helium has long been a limiting factor for nuclear energy development. Low-activation ferritic/martensitic steels—a leading candidate material for future fusion reactors—are primarily composed of Fe-9Cr alloys [1], with major domestic and international compositions shown in .

Under operating conditions, high-energy particle irradiation generates various defects within materials, including vacancies and related atomic defects such as interstitials, dislocations, and dislocation loops [2,3]. These complex structures disrupt the material's internal architecture, consequently degrading irradiation resistance, creep resistance, and other critical properties. Therefore, this study selects helium—the most common dopant in nuclear reactors—to simulate its behavior at Fe-Cr alloy interfaces and conduct computational analysis.

In the field of nuclear materials, researchers have investigated microscopic defects in Fe-Cr alloys primarily through scanning electron microscopy, transmission electron microscopy, and positron annihilation spectroscopy. Studies indicate that Cr atoms in Fe-Cr alloys tend to cluster and form Cr-rich precipitates [10], while appropriate Cr addition can suppress the formation of dislocations and voids [11-13]. Annealing experiments on Fe-9%Cr alloys show that larger microscopic defects gradually disappear when temperatures reach 500°C; as temperature increases further to 800°C, Cr atoms begin to aggregate and form precipitates that eventually dissolve [14]. As the matrix material for fusion reactor first walls, Fe-Cr alloys have been extensively studied experimentally regarding helium migration behavior within microscopic defects using ion implantation, electrochemical methods, and other techniques [15-19]. The inferred helium behavior in Fe-Cr alloys can be summarized as follows: individual or multiple helium atoms entering the material readily combine with vacancies and other helium atoms to form helium bubbles, a phenomenon clearly demonstrated experimentally. This process is accompanied by Frenkel defect pair generation under irradiation. As more helium atoms accumulate, lattice distortion occurs, leading to cluster formation with vacancies and ultimately producing visible helium bubbles that affect the material's physicochemical properties.

This research employs density functional theory through first-principles calculations to accurately determine helium stability at various positions in Fe-Cr interfaces, theoretically establishing how helium atoms at different locations influence interfacial lattice parameters. This provides a theoretical foundation for studying helium migration behavior at nuclear-grade stainless steel interfaces.

1. Computational Methods

First-principles calculations, also known as *ab initio* calculations, consider only fundamental particle interactions and solve the Schrödinger equation using quantum mechanical methods to determine material properties without empirical parameters. The computational software used in this study is the Vienna Ab initio Simulation Package (VASP) [20].

2. Structural Optimization

The optimized structural model consists of an Fe-Cr interface with a body-centered cubic (BCC) structure. Helium doping positions include substitutional sites and interstitial sites (octahedral and tetrahedral interstitials). We performed structural optimization using VASP with the generalized gradient approximation (GGA) for exchange-correlation functionals and the projector augmented-wave (PAW) method [21,22]. Calculations were conducted with ISIF=3 and ENCUT=400 eV until atomic forces converged to less than 0.001 eV/Å. Subsequent static calculations with IBRION=-1 yielded the atomic distribution model at the interface ([Figure 1: see original paper]).

[Figure 1: see original paper]

In the figure, Cr atoms are represented in blue and Fe atoms in yellow. Sections 1, 2, 3, and 4 denote planes parallel to the xoy plane where helium atoms reside. T (Tetrahedron) indicates helium at tetrahedral interstitial sites, O (Octahedron) at octahedral interstitial sites, and S (Supersede) at substitutional sites. For comparison, vacancies are also included: V (Vacancy) represents a substitutional vacancy where a Fe or Cr atom is removed. For example, T3 indicates helium located on plane 3 at the center of a tetrahedron formed by one Cr and three Fe atoms. Based on this optimized structure, helium atoms were placed at these positions and re-optimized using identical parameters, followed by static calculations. Formation energies were calculated using the following formulas [23]:

For interstitial helium:

$$E_{\text{Formation}} = E_{\text{Fe-Cr-He}} - E_{\text{Fe-Cr}} - E_{\text{He}}$$

For substitutional helium:

$$E_{\text{Formation}} = E_{\text{Fe-Cr-He}} - E_{\text{Fe-Cr}} - E_{\text{He}} + E_{\text{single Fe/Cr}}$$

where $E_{\text{Fe-Cr-He}}$ is the total energy of the He-doped Fe-Cr interface system, $E_{\text{Fe-Cr}}$ is the total energy of the pristine Fe-Cr interface, E_{He} is the energy of a single helium atom in an effectively infinite space [24], and $E_{\text{single Fe/Cr}}$ is the static energy of the replaced Fe or Cr atom. The calculated formation energies for helium at various positions in the Fe-Cr interface are shown in [Figure 2: see original paper].

[Figure 2: see original paper]

3. Formation Energy Analysis

The formation energies of V1, V2, V3, and V4 demonstrate that single vacancies created by missing atoms destabilize the Fe-Cr interface structure. Compared to vacancies at Cr sites, vacancies preferentially form at Fe positions away from the interface (V4 position shows the lowest formation energy and highest relative stability). In other words, when a single vacancy forms in the Fe-Cr interface, it tends to occur at Fe atom positions distant from the interface—locations surrounded exclusively by Fe atoms. This provides theoretical guidance for investigating vacancy formation sites in Fe-based alloy reactor materials.

The formation energies of helium atoms at different positions (S1, S2, S3, S4, O1, O2, O3, O4, T1, T2, T3, T4) reveal that helium is most stable at tetrahedral interstitial sites, followed by octahedral interstitial sites, and least stable at substitutional sites. Specifically, helium exhibits the lowest formation energy at the T1 position and the highest at the S1 position. This indicates that upon injection into the Fe-Cr interface, individual helium atoms preferentially occupy Cr tetrahedral interstitial sites far from the interface. With multiple helium atoms, they will fill other tetrahedral sites sequentially, then octahedral sites, and finally substitute for Fe and Cr atoms only after all interstitial sites are saturated. The displaced Fe atoms and helium atoms, due to their larger atomic radii, significantly affect original lattice parameters, creating microscopic defects such as vacancies, vacancy clusters, defect pairs, dislocations, and dislocation loops that further alter material properties.

4. Volume Changes

To more directly assess helium's influence at different Fe-Cr interface positions, first-principles calculations determined the volumes associated with helium and vacancies at various sites ([Figure 3: see original paper]).

[Figure 3: see original paper]

Evidently, both helium and vacancies at substitutional sites reduce the Fe-Cr interface volume compared to the annealed, defect-free interface, with single vacancies causing more pronounced volume reduction. Conversely, helium at interstitial sites significantly increases interface volume. Notably, when helium occupies different positions (O1, O2, O3, O4, T1, T2, T3, T4), the T3 position exhibits substantially larger volume expansion—nearly double that of other positions. This result demonstrates that helium at Fe octahedral interstitial sites near the interface induces substantial lattice distortion, which can alter material dimensions and consequently affect physicochemical properties.

5. Density of States Analysis

To investigate this anomalous behavior, we performed additional high-precision optimizations of the structure with helium at this position, yielding consistent volumes between 358.9 Å^3 and 359.2 Å^3 ($1\ \text{Å} = 10^{-10}$ m). Using p4vasp software, we obtained the total density of states (DOS) and partial DOS for different electronic orbitals, comparing them with those of other octahedral sites (O1, O2, O4) ([Figure 4: see original paper]).

[Figure 4: see original paper]

The electronic density of states reveals electron distribution within specific energy ranges, with DOS profiles reflecting orbital occupations and atomic interactions. While other octahedral sites (O1, O2, O4) show a peak between -20 eV and -18 eV, helium at the Fe octahedral site near the interface (O3) exhibits a peak shifted to -18 eV to -16 eV. This peak shift indicates special interactions between helium and neighboring Cr and Fe atoms. The peak is not attributable to a single atom but represents overlapping contributions from Fe, Cr, and He atoms (red, green, and blue curves), demonstrating orbital hybridization among the three atomic species. However, this configuration remains less stable than other octahedral sites, facilitating helium migration to alternative octahedral or tetrahedral positions.

6. Conclusions

First-principles calculations demonstrate that helium atoms entering Fe-Cr alloy interfaces preferentially migrate to Cr tetrahedral interstitial sites far from the interface, subsequently filling other tetrahedral sites, then octahedral sites, and finally substitutional sites. This sequence provides fundamental insights for investigating helium migration behavior and irradiation resistance in nuclear reactor materials.

Helium atoms at Fe octahedral interstitial sites near the Fe-Cr interface induce significant lattice distortion through specific positional hybridization among He, Fe, and Cr atoms. This distortion substantially alters interfacial atomic arrangements, affecting microscopic defect structures. These findings establish theoretical foundations and research directions for investigating structural impacts of helium at Fe octahedral sites in Fe-Cr interfaces.

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Author Information

First Author: LIAN Xiang-Yu (1993–), male (Han ethnicity), from Linzhou, Henan. Master's degree, Engineer. Research interests include computational simulation, positron annihilation, microscopic defects, and radioactive survey evaluation.

Affiliation: Anhui Nuclear Exploration Technology Central Institute
Correspondence Address: Nuclear Industry Building, No. 8 Zhanghe Road, High-tech Development Zone, Wuhu, Anhui 241000, China

Postal Code: 241000
Phone: 18810901611
E-mail: 312473356@qq.com

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