First-principles Study on the Behaviors of Cr, Mo, and W in the Interfacial Bulk Region of Ni-based Alloys for MSR Applications

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1. Introduction

Fe-based alloys, commonly used in conventional light water reactors (LWRs), have been reported to undergo severe corrosion in molten salt. As an alternative, Ni-based alloys, which have a relatively higher redox potential, are being considered as structural materials for molten salt reactors (MSRs). In fact, Hastelloy N, a Ni-based alloy designed by Oak-Ridge National Laboratory (ORNL) for MSRs applications, has demonstrated significantly lower corrosions compared to Fe-based alloys, as confirmed by several previous studies.

The addition of alloying elements can enhance the corrosion resistance. In the field of MSRs, Ni-based alloys containing Mo and W—both of which have high redox potential—have been studied for their improved performance. [1], [2] However, the effects of alloying elements are not yet fully understood, because they are highly complex, being influenced by atomic interactions, microstructural changes and environmental conditions.

Among them, atomic interactions are challenging to observe through experiments. Therefore, atomistic simulations, combined with experimentally determined diffusivity, offer an effective approach to understanding material behavior at the atomic scale.

In this study, we investigate the behavior of alloying elements (Ni, Cr, Mo and W) in the interfacial bulk region of a Ni-based alloy. Rather than examining direct interface reactions with molten salt, this research focuses on the changes occurring in the interfacial bulk region as alloying elements diffuse toward the interface, with comparing their diffusion tendencies and segregation behaviors.

2. Methods

2.1. Computational details

Among several atomistic simulations, density functional theory (DFT) calculations were performed which can calculate electronic structure using Vienna *ab initio* Simulation Package (VASP).[3] The projector-augmented wave (PAW) method [4], [5] was utilized to treat core electrons, and the Perdew-Burke-Emzerhof (PBE) functional [6] was utilized. The valence electrons were considered as $3d^9 4s^1$, $3d^5 4s^1$, $4d^5 5s^1$, and $5d^5 6s^1$ for Ni, Cr, Mo and W, respectively. The cutoff energy was set to 400 eV for the plane-wave basis set and the first-order Methfessel-Paxtons's smearing method [7] was used with a smearing width of 0.2 eV. The spin-polarized calculations were conducted to account for magnetism. All calculations were performed in 3×3×3 fcc supercells (108 atoms), with k-points sampling on a 3×3×3 Γ-centered mesh.

In this study, calculations were performed for Ni-Cr, Ni-Cr-Mo and Ni-Cr-W alloys. The concentration range for each alloying element was systematically varied to cover practical compositions relevant to MSRs applications. Specifically, the Cr content ranged up to 12 wt %, Mo up to 27 wt% and W up to 33 wt%.

The atomic configuration was set by substituting randomly selected Ni atoms with alloying elements in the fcc structure. Since random configurations were used, five samples were generated for each chemical composition. Subsequently, geometry optimizations were performed by adjusting both the atomic positions and the cell parameters, including volume and shape. The calculations were completed when the system energy difference from a previous step becomes less than 1.0×10^{-3} eV.

2.2. Mixing energy

The mixing energy of each alloy was calculated using the following equation:

$$E_{mix} = E_{alloy} - \sum_i^N n_i E_{i,fcc}, \qquad \text{eq. (1)}$$

where E_{alloy} denotes the total energy of the alloy, n_i is the number of atoms of the *i* alloying element, $E_{i,fcc}$ is the energy of *i* elements in a pure fcc structure and i denotes Ni, Cr, Mo, and W depending on the alloy composition. This mixing energy is defined with respect to pure metals in the fcc structure and indicates whether alloying elements become more stable or unstable upon mixing. If the value is negative, the mixing process stabilizes the alloy relative to the pure fcc metals. Conversely, if it is positive, mixing leads to instability of the alloy.

2.3. Formation energy

The formation energy was calculated as

$$E_f = E_{alloys} - \sum_i^N n_i E_{i,j}, \qquad \text{eq. (2)}$$

where $E_{i,j}$ is the energy of i elements in its most stable crystal structure, j. This formation energy is referenced to the most stable crystal structures of pure elements, distinguishing it from mixing energy. Specifically, Ni has an fcc structure while Cr, Mo, and W have bcc structures as their stable phases.

The formation energy represents the phase stability of an alloy. If the energy is negative, it means the alloy is energetically stable. If it is positive, the alloy is less stable, suggesting tendency toward phase separation or decomposition. Additionally, by comparing alloy formation energies at different compositions, we can assess which system is relatively more stable.

3. Results and Discussion

3.1. Alloys stability

Although Mo, Cr, and W adopt a bcc structure (Table 1), the mixing energy calculations in this study were performed assuming an fcc structure for all elements. This approach facilitates comparison with ideal thermodynamic models, where ideal mixing behavior is often considered within the same crystal structure. While the absolute values may differ from real systems, the observed decreasing trend in mixing energy aligns with the typical behavior expected in ideal thermodynamic models where mixing energy generally decreases with increasing alloying element concentration up to 50 wt%. Additionally, since W and Mo have a larger atomic radius than Ni (Table 2), their addition leads to an increase in the system volume. These results imply that the simulations can reflect realistic material behavior and can be utilized to capture the fundamental mechanism governing alloy stability.

Since the formation energy was calculated based on the fcc structure for Ni and the bcc structure for Cr, Mo and W (Table 1), it exhibits a different trend from the mixing energy. Formation energy enables the evaluation of the relative stability of different alloy compositions. A key observation is that Cr exhibits a distinct trend compared to Mo and W. While the addition of Cr increases the formation energy, Mo enhances stability in the 10-20 wt% range, whereas W contributes to the highest stability in the 20-35 wt% range, particularly at low Cr concentrations.

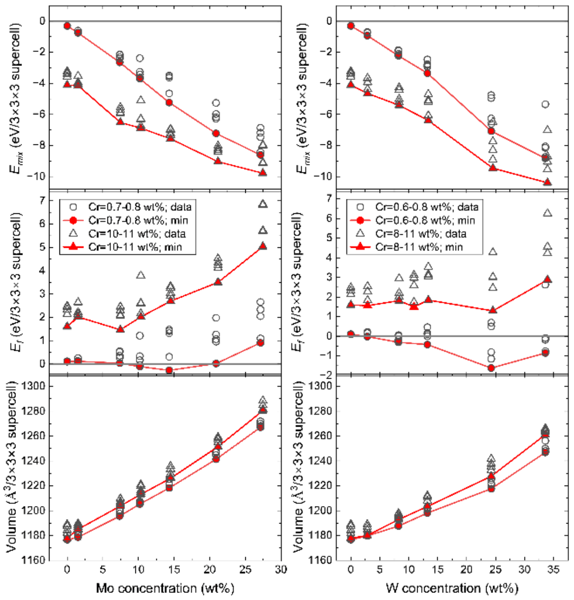

Figure 1. The mixing energy, formation energy and volume of the alloys with respect to Cr, Mo, and W concentrations.

Table 1. Cohesive energy per atom of Ni, Cr, Mo and W in bcc and fcc structures.

$E_{cohesive}$ (eV/atom)	Ni	Cr	Mo	W
bcc	2.279	5.475	8.351	8.492
fcc	5.064	5.065	7.891	7.992

3.2. Diffusion of the alloying elements

The diffusion of alloying elements is one of the key factors influencing corrosion mechanisms. Table 2 presents the self-diffusivity of pure Ni and the diffusivities of Cr, Mo, and W in Ni-based alloys, determined experimentally. Although the data at 650 °C were extrapolated using an Arrhenius plot, both the 650 °C and 900 °C data reveal that Cr and Mo exhibit the highest diffusivities, followed by Ni. W shows the lowest diffusivity, over an order of magnitude lower than the others, implying that W rarely diffuses.

Table 2. The atomic radius[8] **and experimental diffusivity at 650 °C and 900 °C for each element. Diffusivity for Ni is from the reference**[9] **and diffusivity of Cr, Mo, and W are from the reference** [10], [11]**. Please note that the diffusivities at 650 °C are extrapolated values from Arrhenius plot, while the those at 900 °C are in interrelation.**

	Atomic radius (Å)	Diffusivity at 650 °C (m^2/s)	Diffusivity at 900 °C (m^2/s)
Ni	1.24	1.72×10^{-20}	4.19×10^{-17}

Cr	1.28	3.68×10^{-20}	9.79×10^{-17}
Mo	1.39	5.08×10^{-20}	8.56×10^{-17}
W	1.39	3.03×10^{-21}	7.64×10^{-18}

3.3. Alloying element migration in interfacial bulk region

Due to molten salt corrosion, alloying elements become depleted, causing the elements present in the interfacial bulk region to begin diffusing towards the interface, following the vacancy concertation gradient. The corrosion behavior of each alloying element can be explained based on the phase stability of Ni-based alloys and their diffusion characteristics.

Cr, with its high diffusion coefficient, rapidly migrates to the surface. However, due to its low redox potential and the fact that lower Cr content favors alloys stability, Cr is likely to be quickly and continuously leached into the molten salt at the interface.

Mo also exhibits a high diffusion coefficient, enabling rapid migration towards the interface. In contrast to Cr, its higher redox potential results in less depletion. Additionally, as Ni–Cr–Mo alloys tends to stabilize within the 10-20 wt% Mo at low Cr concentration, the surface segregation of Mo may occur when its content is lower than this range.

For W, phase stability is achieved within the 15-30 wt% range, and it possesses a high redox potential. However, due to significant lower diffusion coefficient, W exhibits minimal migration toward the surface, and thus, segregation is unlikely to occur.

These results suggest that Cr tends to undergo depletion as its concentration increases. Given that Cr must be included to protect the air-facing side of alloys from oxidation, Ni-based structural materials for MSRs applications should be designed to suppress the depletion of not only Ni but also Cr.

Mo and W are identified as promising alloying elements that may contribute to reducing the depletion. While the current study focused on segregation behavior based on phase stability and diffusion coefficients, further investigations are planned to clarify their specific roles in mitigating elemental depletion.

4. Conclusions

In this study, DFT-calculated phase stability and experimental diffusivity were utilized to explain the diffusion and segregation behavior of Cr, Mo, and W in the interfacial bulk region of Ni-based alloys.

It should be noted that this study did not address the competitive migration behavior of Ni, Cr, Mo, and W towards the surface, nor did it consider the corrosion behavior associated with grain boundaries (GBs), secondary phases, and temperature variations—highlighting a limitation of this work. Accordingly, a direct correlation between the present findings and corrosion resistance is beyond the current scope and will be investigated in subsequent studies.

Future work will explore competitive surface migration behavior using surface energetics and migration barriers through atomistic simulations. Aiming to provide a deeper understanding of the underlying corrosion mechanisms.

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