Current Status of Molecular Dynamics Simulation of Corrosion in Reactor Alloys

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Abstract

The corrosion of reactor alloy materials directly affects reactor service safety and lifespan, and has consistently received significant attention and extensive research. However, relying solely on experiments is insufficient to elucidate corrosion mechanisms and difficult to achieve high-precision predictions of corrosion behavior. With the development of computational materials science, simulation has emerged as a new approach for investigating corrosion of reactor alloy materials. The molecular dynamics method, capable of handling scales of tens of thousands to hundreds of thousands of atoms, is suitable for simulating various surface and interface behaviors of materials; consequently, it has found certain applications in the research of corrosion mechanisms of reactor alloy materials in recent years. This review covers two aspects: first, an introduction to molecular dynamics methods and potential functions suitable for corrosion simulations, mainly including reactive force field, tight-binding quantum chemical force field, and machine learning force field, etc.; second, a survey of the current research status on corrosion of reactor alloy materials in water-cooled reactors, liquid metal cooled reactors, and other environments using molecular dynamics methods, including corrosion behaviors such as grain boundary element segregation, solid-liquid interface adsorption, and stress corrosion cracking.

Full Text

Preamble

A Review of Molecular Dynamics Simulation for Corrosion of Reactor Alloy Materials

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Abstract

Corrosion of reactor alloy materials is directly related to the safety and lifetime of nuclear reactors and has received great attention and extensive research. However, experiments alone are insufficient to clarify the corrosion mechanism and difficult to predict corrosion behavior with high accuracy. With the development of computational materials science, simulation has become a new tool in reactor alloy material corrosion research. Molecular dynamics methods can handle tens to hundreds of thousands of atoms and are suitable for simulating various surface and interfacial behaviors of materials, so they have found numerous applications in the field of reactor alloy material corrosion mechanism research. This paper reviews two main aspects: first, an introduction to molecular dynamics methods applicable to corrosion simulation calculations, mainly including reactive force field, tight-binding quantum chemical force field, and machine learning force field; second, the current status of corrosion research using molecular dynamics methods to study reactor materials in water-cooled reactors, liquid metal-cooled reactors, and other environments, including grain boundary element segregation, solid-liquid interface adsorption, and stress corrosion cracking.

Keywords: Reactor alloy materials, Corrosion simulation, Molecular dynamics, Interaction potential, Corrosion behavior

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Introduction

Corrosion of reactor alloy materials directly affects reactor service safety and lifetime, and has therefore attracted significant attention. To investigate corrosion failure of reactor alloys, numerous experimental studies have been conducted over several decades, including extensive research on corrosion of common reactor materials such as stainless steel, nickel-based alloys, aluminum alloys, and zirconium alloys. These efforts have yielded substantial experimental data and corrosion patterns that provide valuable guidance for alloy service in reactors. Reactor alloy materials may experience several severe corrosion forms during service [1], including pitting, stress corrosion cracking (SCC), and corrosion fatigue. Because corrosion behavior is typically influenced by multiple factors, predicting corrosion of reactor alloy materials remains challenging. Clarifying the corrosion mechanisms is essential for accurate prediction of corrosion behavior. Although long-term experimental research has provided some understanding of corrosion mechanisms, corrosion is a complex process involving multiple coupled factors, and thermodynamic and kinetic laws derived from traditional experiments alone cannot clearly reveal its mechanisms.

With the rapid development of computer technology, computational materials science has become a prominent research direction in materials science, and simulation methods have emerged as new tools for investigating material corrosion behavior and mechanisms [2-4]. Molecular dynamics (MD) is a method for simulating the motion of individual particles in many-particle systems (solids, liquids, gases). By integrating thermodynamics and statistical mechanics theory, MD simulations can derive macroscopic properties of material systems. This method is suitable for simulating various material surface and interface behaviors, with simulation scales spanning tens to hundreds of thousands of atoms. In recent years, MD simulation has found increasing application and attention in reactor alloy material corrosion mechanism research. However, the reliability of MD simulations depends on the accuracy of the potential function, and developing a potential function that matches the system quickly and accurately remains an important challenge in MD simulation research.

This paper introduces MD simulation methods and commonly used potential functions, and summarizes their applications in simulating corrosion of reactor alloy materials in various environments.

1. Molecular Dynamics Simulation Methods

MD simulation is a molecular force field-based method that predicts various physicochemical properties of a system through sampling of microscopic models. The MD method simulates the motion of individual particles in many-particle systems (solids, liquids, and gases), with its theoretical foundation in Newtonian mechanics. The key task is to obtain particle motion information—namely, the position and velocity of particles at different times. Based on the calculated particle motion information, statistical and thermodynamic methods can be used to obtain properties of many-body systems and derive macroscopic properties. MD is based on classical mechanics (which primarily studies particles, forces, and motion), i.e., Newtonian mechanics. Under the Born-Oppenheimer approximation [5], a molecule's energy can be approximated as a function of the spatial coordinates of its constituent atomic nuclei. There exists a mapping relationship between atomic coordinates and molecular energy, which can be described by a potential function. The MD simulation process involves solving Newton's equations of motion for a many-body atomic interaction system, performing numerical integration of the equations of motion over very short time steps to obtain the time evolution of atomic positions and energies in the system. During simulation, assuming N is the number of atoms in the system, the mass of the i-th atom is m_i, its position coordinate vector is r_i, its distance from the j-th atom is $r_{ij} = |r_i - r_j|$, the atomic force is expressed as F_i, and the potential energy of the atom interacting with atoms within the cutoff radius r_c is U_i, given by:

$$m_i \ddot{r}_i = F_i = -\nabla_i U_i$$

Here, the interatomic interaction force is expressed as the negative gradient of the interaction potential, establishing the relationship between atomic positions and forces. Therefore, given initial positions and velocities, the position and velocity of any atom in the system at any time can be obtained using numerical integration methods on a computer. Additionally, in actual MD simulations, process parameters such as boundary conditions and ensembles must be set according to the characteristics of the target system, as shown in Figure 1 [Figure 1: see original paper].

The origin of MD simulation methods can be traced back to 1957, when Alder et al. [6] used MD with a hard-sphere model to study the equations of state for gases and liquids. For MD simulations, the potential function describes interatomic interactions and directly affects simulation accuracy. Since potential functions are often empirical or semi-empirical, their accuracy in describing different material systems varies due to differences in functional construction. Consequently, MD methods are divided into various types. Although MD simulation objectives may vary according to individual interests, they are typically aimed at obtaining equilibrium properties of systems. In reactor structural material corrosion research, the special electronic environment of metals must be considered. To describe interatomic interactions in metal systems, Daw et al. [7, 8] proposed the Embedded Atom Method (EAM) potential function in 1984, which has been widely applied in metallic material corrosion research. Additionally, to account for adsorption and chemical reactions during corrosion, other force fields capable of describing surface adsorption and interface diffusion are widely employed. In 1998, Sun et al. [9] developed a universal all-atom force field (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies, COMPASS) for atomistic simulations of common organic molecules, inorganic small molecules, and polymers. In 1999, YAMADA et al. [10] created a Tight-binding Molecular Dynamics (TBMD) potential function and studied the desorption behavior of SiO molecules during high-temperature oxidation of Si(111) surfaces. Furthermore, in 2001, Van Duin et al. [11] proposed a bond-order-based reactive force field (Reactive Force Fields, ReaxFF), particularly suitable for describing chemical reaction processes. In 2003, Cygan et al. [12] developed the CLAYFF (Clay Force Field) force field based on ionic (non-bonded) relationships for metal-oxygen interactions, applicable to molecular simulations of hydrated crystalline compounds and their interfaces with fluid phases.

In recent years, with advances in computer technology, the advantages of MD simulation in computational efficiency and atomic scale have become more prominent. However, issues of transferability and representability remain to be solved. To overcome the limitations of traditional MD, researchers have considered obtaining interatomic interaction potentials directly from quantum mechanics (QM) orbital theory. Based on whether QM effects are considered, MD potentials can be divided into classical force fields, semi-empirical force fields, and Machine Learning Potentials (MLP). A reasonable potential function is a necessary condition for molecular dynamics simulation. Before using non-dedicated potentials, validation is required to determine their suitability for the current simulation system.

1.1.1 Lennard-Jones Potential Function

In the early stages of MD development, pair potentials were the main form of physical potential functions, including discontinuous pair potentials [6] and continuous pair potentials (Lennard-Jones potential [13], Morse potential [14], etc.).

Discontinuous pair potential:

$$E = \{E(r_{ij}), \quad r_{ij} < r_0\}$$

A discontinuous pair potential means that when the interparticle distance exceeds a certain value, the pair potential becomes zero.

Lennard-Jones potential:

$$V(r_{ij}) = 4\varepsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}]$$

Morse potential:

$$V(r_{ij}) = Ae^{-2B(r_{ij}-r_0)} - 2Ae^{-B(r_{ij}-r_0)}$$

where A, B, and r_0 are parameters to be determined. The construction of pair potentials is relatively simple, with the first term in the interaction expression representing repulsive effects and the second term representing attractive effects. The Lennard-Jones potential contains only two parameters—one representing the depth of the potential well and one representing the equilibrium atomic spacing—making its accuracy far from sufficient for precise calculations. For classical MD, applicability and accuracy are often contradictory. The Morse potential is a three-parameter exponential potential energy function suitable for diatomic molecular systems. Building on the Lennard-Jones parameters, the Morse potential adds a parameter controlling the width of the potential well and includes information about bond breaking, enabling calculation of vibrational properties within the system. The Born-Mayer potential, proposed by M. Born and J. E. Mayer [15] in 1931, is a potential energy function for describing ion interactions in ionic crystals. Pair potential functions describe neutral atom and molecular systems well, but the metal crystal models they establish are not accurate enough, particularly showing significant differences from reality in describing crystal elasticity. Two-body interaction potentials represented by the LJ potential have simple construction forms and are convenient for fitting, usable for describing noble gas elements. However, such potential functions completely ignore electron behavior and can only provide rough simulations. They have certain value in describing mixed potentials or uncommon elements, but their predictive accuracy is extremely limited for reaction processes involving electron exchange.

Arkundato's team simplified liquid metal systems and used the Lennard-Jones potential to study the diffusion performance of corrosion inhibitors in liquid metals.

1.2.1 Embedded Atom Method Molecular Dynamics

The EAM potential function primarily describes the repulsive interaction between atomic nuclei and the electrostatic interaction between atomic nuclei and surrounding electrons and other electrons. The EAM potential function is defined as [7, 8]:

$$E_{\text{EAM}} = \sum E(\rho_i) + \sum \phi(r_{ij})$$

where E_{EAM} represents the total system energy, which includes embedding energy and two-body potential components. The first term represents the embedding energy required to embed atom i into the electron cloud of atom j, while the second term represents the two-body potential between atoms i and j separated by distance r. Model parameters are optimized by fitting basic physical quantities of complete pure metal systems, such as lattice constants, sublimation energies, elastic constants, and vacancy formation energies. In the modified embedded atom method, the total system energy is expressed as the sum of embedding atomic potential and electrostatic potential [16, 17]. This method has been applied in liquid metal corrosion research. Additionally, Zhou et al. [18] proposed the Generalized Embedded Atom Method (GEAM) in 2001, which can better describe many-body interactions and has been successfully applied to diffusion property studies of metals and alloys.

The construction of the EAM potential function includes embedding energy and two-body potential terms, where the embedding energy term can effectively fit the electronic properties of metal elements, playing a significant role in pure metal and alloy simulations. However, the EAM potential function shows poor fitting effects for non-metal elements, so it is often mixed with LJ or other potential functions in corrosion reaction simulations. Due to the low computational complexity of EAM, its model size can reach hundreds or even thousands of nanometers, offering certain advantages for handling crack propagation or hydrogen embrittlement problems in metal matrices.

1.2.2 Reactive Molecular Dynamics

Reactive Force Fields Molecular Dynamics (ReaxFF-MD) is an MD simulation method that combines the bond order concept with an electronegativity equalization scheme. In recent years, it has demonstrated strong capabilities in studying metal oxide systems and energetic material systems. In this potential function, bond order is expressed as a function of interatomic distance:

$$BO(R_{ij}) = BO_{ij}^{\sigma} + BO_{ij}^{\pi} + BO_{ij}^{\pi\pi}$$

This enables simulation of bonding-related interactions within chemical systems using atomic coordinates, particularly allowing smooth energy transitions during bond formation and breaking.

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{lp}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{vdW}} + E_{\text{Coul}} + E_{\text{H-bond}}$$

where E_{vdW}, E_{Coul}, and $E_{\text{H-bond}}$ represent van der Waals forces, Coulombic forces, and hydrogen bonds, respectively; E_{bond} represents bond energy; E_{val} represents bond angle energy; E_{lp} represents lone pair electron energy; and E_{over} and E_{under} represent atomic over-coordination and under-coordination terms.

During simulation, atomic charges in the system are dynamically optimized at each time step using the electronegativity equalization method. Atomic charges are related to the system's geometric positions. This calculation process is computationally intensive in ReaxFF-MD simulations, enabling better description of polarization effects [19]. ReaxFF-MD calculations have significantly lower complexity than first-principles calculations while maintaining similar accuracy. Moreover, ReaxFF-MD is a method completely driven by system potential energy, requiring no preset reaction paths when studying reaction mechanisms, which helps explore complex reaction mechanisms and corrosion product behavior. Although this potential function shows no obvious preference for element types, its construction form is relatively complex, and its fitting complexity increases significantly with the number of elements accommodated, making development difficult.

1.2.3 Tight-Binding Molecular Dynamics

Traditional MD simulation methods cannot provide any information about electronic structure and are unsuitable for simulating chemical reaction processes. TBMD simulation is a quantum chemistry-based simulation method [20-22]. The tight-binding model is a method for describing electronic structure based on overlap and interaction between atomic orbitals. In TBMD, this electronic structure model is applied to simulate the dynamic behavior of molecular systems. It describes atomic potential energy as the sum of atomic kinetic energy, valence electron orbital energy, Coulomb interaction between core charges, and short-range repulsive forces between atoms. In the TBMD program "Colors," the total energy between any pair of atoms designated as i and j is given by the expression:

$$E = \sum \frac{1}{2} m_i v_i^2 + \sum \sum \epsilon_n + \sum \sum \frac{Z_i Z_j e^2}{R_{ij}} + \sum \sum E_{\text{rep}}(R_{ij})$$

where the first, second, third, and fourth terms represent kinetic energy, the sum of electronic energies of all occupied orbitals (valence electron orbital energies), Coulomb interaction energy, and exchange-repulsion interaction energy, respectively. Here, m and v are atomic mass and velocity, Z_i and Z_j are atomic charges, e is the elementary charge, and R_{ij} is the internuclear distance. Model parameters such as valence state ionization potentials of atomic orbitals and

Slater exponents of atomic orbitals are determined using first-principles methods to achieve high accuracy. This method offers higher computational efficiency compared to first-principles molecular dynamics. However, TBMD computational speed is still several orders of magnitude slower than other potential functions. This potential function shows no obvious bias toward elements and can accurately calculate energy issues during surface adsorption and diffusion processes, making it suitable for simple corrosion reaction simulations.

1.3 Machine Learning and Molecular Dynamics Simulation

Machine learning is a science that learns patterns from existing datasets and uses the acquired patterns to make predictions in unknown domains. In computational chemistry, machine learning can completely numericalize parts of real chemical problems that cannot be precisely explained by existing theoretical models. It can infer potential relationships between abstract physical laws and complex chemical processes, significantly expanding the application scope of computational chemistry and promising to solve the dilemma of balancing accuracy and efficiency in existing computational methods. For trained data domains, pure numerical models have high prediction accuracy and low computational complexity. When used to predict unknown domains, the model's extrapolation capability requires sufficient validation. Therefore, in machine learning, attention must be paid not only to model accuracy and complexity but also to its adaptability and generalization capability to ensure reliable predictions for new data.

In machine learning potentials, system energy is described as the sum of contributions from all atoms:

$$E_\omega = \sum E_i = \sum E_i(\omega(R_i))$$

In fact, unlike completely numericalized models, a system's energy satisfies a series of symmetry requirements, meaning the mapping relationship from system coordinates to energy and forces must satisfy certain symmetries. To address the physical expression problem of machine learning functions, researchers introduced the concept of descriptors:

$$D(R_i) = D(UR_i) \quad \forall U \in u$$

A descriptor is a mapping of atomic coordinates that satisfies all symmetry requirements and has sufficient resolution. Currently commonly used descriptors include symmetry function descriptors [23], smooth overlap [24], Coulomb matrices [25], SchNet, and convolutional descriptors [26, 27].

After finding suitable descriptors, the energy contribution of the system can be expressed as:

$$\omega(R_i) = F(D(R_i))$$

where F represents the fitting method, which is often chosen as linear functions, kernel functions [24, 25], or neural networks [26, 27] according to different fitting requirements.

Machine learning potentials directly construct potential functions using high-dimensional representation capabilities. Through the powerful representation ability of high-dimensional functions, interaction potentials for complex multi-component systems are modeled to obtain high-precision accelerated molecular dynamics force fields.

The German Schütt team [28, 29] used continuous filter convolutional layers as a new building block for deep neural networks. Unlike general convolutional layers, SchNet can model non-uniformly spaced data that appears in quantum chemistry. Yoo et al. [30] developed a neural network reactive force field (NNRF) for carbon, hydrogen, oxygen, and nitrogen systems to describe decomposition and reactions of energetic materials. NNRF was trained using energies and forces from a total of 3100 molecules (11,941 geometries) and 15 condensed-phase systems (32,973 geometries) obtained from density functional theory calculations with semi-empirical corrections for dispersion interactions.

For the development of machine learning potentials, training set construction is crucial. A good training set can greatly shorten the potential development process and has a decisive impact on potential accuracy. The Gil team [31] designed an automated workflow using machine learning moment tensor potentials to effectively calculate the solution enthalpy and diffusivity of solutes in liquid metal Na. After training and testing, this method can achieve accuracy comparable to direct first-principles molecular dynamics calculations while significantly reducing computational costs by 1-10 to 1-100 orders of magnitude. The process uses first-principles calculation software VASP to compute data for model training, followed by LAMMPS for simulation comparison. The general development process for machine learning force fields is shown in Figure 2 [Figure 2: see original paper].

For classical MD, developing dedicated potentials consumes significant human and time resources. Machine learning can quickly and accurately solve the parameter optimization problem for empirical or semi-empirical potentials. Sengul et al. [32] proposed a deep learning-based optimization framework (INDEEDopt) to accelerate the ReaxFF parameterization process. This work fully leverages the advantages of machine learning methods for parameter optimization and was tested on Ni–Cr and W–S–C–O–H training sets with good results. Compared with other potentials, machine learning potentials have far fewer restrictions on element types and are more suitable for simulating corrosion behavior in multi-element systems, such as molten salt cooling environments or high-entropy alloy materials.

Currently, MLP has been used to study various properties of reactor alloy materials, including diffusivity [31, 33, 34]. These studies have demonstrated that MLP can compensate for the accuracy limitations of classical MD simulations while enabling large-scale simulations at relatively fast speeds, showing great potential in reactor alloy material corrosion simulation. As pure mathematical models, when the training set is appropriate, MLP can achieve near-first-principles accuracy in predicting energy and forces (provided the atomic configuration has sufficient similarity with some known configurations in the training database). However, for less familiar atomic environments, energy or force predictions are based on pure mathematical extrapolation models, which often lack physical meaning, making reliability difficult to guarantee and potentially producing incomprehensible simulation phenomena.

2. MD Simulation of Reactor Alloy Material Corrosion

Based on different coolant media, reactors are mainly divided into water-cooled reactors, liquid metal-cooled reactors, molten salt reactors, and gas-cooled reactors. The corrosion behavior and mechanisms of materials differ in various media environments. This section reviews the current status of MD simulation research on corrosion of reactor alloy materials in water, liquid metal, and other environments.

2.1 Material Corrosion Simulation in Water-Cooled Reactor Environments

Water-cooled reactors are currently the most widely used reactor type. Reactor internals and steam generators in water-cooled reactors commonly use stainless steel and nickel-based alloy materials, while fuel assemblies primarily use zirconium alloys. These materials all face corrosion problems in high-temperature, high-pressure water environments. Over the past decade, domestic and foreign researchers have conducted simulation studies to explore corrosion mechanisms of water-cooled reactor alloy materials, as detailed in Table 1 . Because developing interaction potentials for multi-element systems is relatively difficult, researchers often use one or several main elements for modeling to simplify simulations and study corrosion mechanisms.

Iron, as the most common metal element in alloy materials, has received considerable attention in Fe-H_2O system corrosion simulation, with applicable potential functions for describing corrosion reactions continuously updated. For example, the ReaxFF for iron oxyhydroxide systems developed by Aryanpour et al. [35] (named Aryanpour-2010) has been widely used to simulate corrosion behavior in Fe-H_2O or Fe-O systems. Additionally, Liu et al. [36] and Jiang et al. [37] extracted Fe-O-H parameters from the Shin-2012 reactive force field to form mixed force fields for Fe-Cr-Ni-O-H and Fe-Cr-O-H, respectively, to study corrosion processes of stainless steel with water. In fact, for MD simulations, extracting the main influencing factors from actual processes to simplify computational complexity is crucial. Therefore, systems containing Fe, O, and H are fundamental for studying Fe-H_2O corrosion processes.

Ren et al. [38] used COMPASS II [48] to simulate Fe_3O_4 migration behavior based on fouling problems on the outer surface of steam generator heat transfer tubes under pressurized water reactor secondary loop conditions. The study found that temperature and concentrations of Fe^{2+} and OH^- not only affect the agglomeration size of Fe_3O_4 deposits on surfaces but also cause differences in diffusion coefficients of Fe^{2+} and OH^-. Additionally, a double-layer structure on the oxide surface was observed during simulation.

To more accurately describe the Fe-H_2O reaction process, Huang et al. [3] established an improved Fe-H_2O reactive force field based on existing Fe-H_2O potentials. This study added descriptions of H and O diffusion behavior in the Fe matrix to existing reactive force fields, enabling more precise reproduction of Fe corrosion mechanisms in supercritical water. Regarding surface corrosion processes, Huang et al. believed that differences in water dissociation energy on different surfaces significantly affect initial corrosion rates, but as the reaction progresses, O atom diffusion rate becomes a more critical factor driving oxide layer formation. Simulation results also indicated that oxide growth occurs from the metal-water interface outward, forming an outer porous Fe_3O_4 layer and an inner dense FeO layer. This potential function can be used to study not only uniform surface corrosion but also corrosion behavior at grain boundaries. Xiao et al. [39] simulated Fe-H_2O interface corrosion behavior at different grain boundaries based on the new Fe-H_2O reactive force field. Simulations of single crystal, twin crystal, and polycrystalline grain boundaries showed that stress concentration phenomena destroy the ordered structure of the original metal matrix, generating numerous vacancies that provide diffusion channels for elements at grain boundaries. Among these, polycrystalline grain boundaries create more complex stress distributions and more obvious stress concentration, and stress release in high-stress zones during corrosion promotes rapid O atom penetration into grain boundaries to form oxides, leading to intergranular corrosion in pure iron.

Besides studying metal matrix-water reactions, Fe-O-H systems can also simulate interactions between iron oxides or hydroxides and water. Svishchev et al. [40] studied adsorption behavior of supercritical water on ferrous hydroxide surfaces through MD simulations. The research showed that temperature and density of supercritical water affect the properties of adsorption layers on ferrous hydroxide surfaces. Although their densities and specific densities differ significantly, local aggregation phenomena uniformly appear. Subsequently, Kallikragas et al. [41] supplemented the study of how interstitial size in ferrous hydroxide systems affects diffusion performance of water molecules and chlorine atoms. Results showed that water molecules are significantly affected by hydration, exhibiting maximum diffusion coefficients in 80 Å gaps, but when temperature increases to a certain level, hydration effects become negligible and gap influence weakens. For chlorine atoms, gap size has little effect.

In addition to conventional corrosion problems, the Fe-H_2O system has also been used to explore complex multi-factor coupled corrosion cracking problems. Huang et al. [2] studied SCC cracking of α-Fe in supercritical water, proposing that SCC results from the coupling effect of hydrogen embrittlement and intergranular corrosion. Their simulations showed that Fe atoms near grain boundaries are preferentially oxidized, while stress concentration occurs in hydrogen-enriched zones beneath grain boundary oxide layers. Additionally, numerous vacancies at grain boundaries promote O atom diffusion, accelerating intergranular corrosion processes and reducing grain boundary cohesion, ultimately leading to intergranular cracking.

In stainless steel materials, Cr and Ni elements play key roles in corrosion resistance. Therefore, interaction potentials containing Cr, Ni, and other elements have been developed to study the effects of alloying elements on corrosion.

Suzuki et al. [42] used TBMD to simulate the initial oxidation stage on Fe and Fe-Cr alloy surfaces. Simulation results showed that surface chromium atoms separate from the surface and combine with oxygen atoms faster than iron atoms, preferentially forming Cr-O bonds. In reality, surface corrosion processes are much more complex, with grain boundaries, stress, and element diffusion coupling together to influence corrosion behavior. Therefore, Das et al. [43] studied corrosion processes at three grain boundaries in Fe-Cr binary alloys. Initially, water molecules adsorbed on the surface and gradually decomposed into O, H, and OH. O and OH ions smoothly penetrated at $\Sigma3(111)$ and $\Sigma5(100)$ grain boundaries, while random grain boundaries hindered diffusion of these species. Subsequently, O and OH concentrations around chromium at grain boundaries increased, preferentially forming Cr-O bonds that remained at grain boundaries, demonstrating preferential grain boundary oxidation. More chromium atoms then migrated to grain boundaries while iron atoms moved outward. Additionally, they applied stress to both sides of the metal surface, but this stress was far below the threshold stress for SCC cracking, serving only to accelerate intergranular corrosion.

However, TBMD simulates relatively small systems over short timescales. To obtain more pronounced water corrosion behavior of Fe-Cr binary alloys, Xu et al. [44] used the ReaxFF force field developed by Shin et al. [49] to study oxidation behavior of Fe-Cr binary alloys in supercritical water. This study considered atomic diffusion at the metal-inner oxide interface, inner oxide-outer oxide interface, and outer oxide-supercritical water interface, reproducing the formation process of double-layer oxides. Initial corrosion behavior was consistent with Das et al.'s research, with Cr atoms showing higher priority for oxygen combination. Xu et al. believed that once the initial oxide layer forms, subsequent oxide growth depends on atomic diffusion rates within the oxide layer. At the oxide-steam interface, O atoms diffuse inward while Fe atoms diffuse outward, maintaining the oxidation process. Fe atoms combine with steam products to form outer iron oxides, while O atoms diffuse inward to form inner iron oxides. Additionally, some substances in the form of $Cr(OH)_4$ could form on FeCr alloy surfaces, consistent with experimental observations [50]. This structural morphology is attributed to the stronger binding energy between Cr atoms and nearest-neighbor oxygen atoms.

After understanding alloy surface corrosion processes, Das et al. [21] used TBMD to study SCC crack initiation in FCC Fe-Cr-Ni ternary alloys at 288°C. Prior to this, SCC in Fe and Fe-Cr binary systems had also been studied [37, 51]. Research showed that Ni atoms also tend to migrate toward the surface but do not easily leave the matrix, instead potentially forming Ni-enriched zones at crack tips that reduce O atom diffusion rates in these regions. Additionally, hydrogen diffusing into deeper metal layers becomes negatively charged after obtaining electrons from metal atoms, weakening metallic bonds and making it easier for O to diffuse to the surface. Hydrogen effectively acts as an oxygen carrier, an insight also reflected in other studies [2, 3, 37]. Nickel-based alloys and stainless steel share the same main metallic elements, meaning MD simulation approaches will have many similarities. Liu et al. [36] used reactive force fields to simulate SCC behavior of Ni60Cr30Fe10 alloy in 900 K dissolved oxygen water, studying the effects of compressive cold working deformation and grain boundary structure on SCC. Previously, ReaxFF-MD had been successfully applied to study SCC initiation behavior in Ni single crystals and Zr bicrystals [52-54]. Liu et al. believed that crack formation is primarily driven by local shear stress/strain and atomic stress from intergranular oxidation, and their study of slip band and twin band motion in metal matrices partially corroborated the slip-dissolution model of SCC. Their simulations also observed diffusion of iron hydroxide molecules from the surface to the solution and deposition back to the surface, confirming the phenomenon of iron hydroxide precipitation onto Ni60Cr30Fe10 alloy oxide surfaces in high-temperature water.

In addition to the corrosion problems of water reactor structural materials mentioned above, zirconium cladding corrosion behavior can also be studied using MD. Mark et al. [55] proposed a charge-optimized many-body potential for zirconium, hydrogen, and oxygen systems and simulated adsorption and dissociation processes of O_2 and H_2O molecules on zirconium metal surfaces. In fact, experimental studies have found that zirconium oxide is a good hydrogen barrier, meaning most hydrogen diffusion into metal occurs before the zirconium oxide achieves perfect structure. Hu et al. [45] studied zirconium oxide formation and hydrogen diffusion processes, with this work covering both experiments and calculations—a typical case of extracting problems from experiments and supplementing them with simulation calculations. Researchers found during experiments that zirconium alloy corrosion in aqueous environments produces nanopores and nanotubes in the initial stage, with extensively interconnected nanotubes found in the non-protective outer oxide layer, while continuous nanotubes become individual nanopores in the protective barrier layer closer to the metal-oxide interface. To address this issue, Hu et al. studied the effect of O vacancies on H diffusion through computational simulation and constructed a zirconium oxide model containing nanotubes. Simulation results showed that H_2 molecules diffuse from the oxide-liquid interface to the oxide interior and even to the oxide-metal interface through constructed nanochannels. Additionally, it was found that when channels are sufficiently large, H_2O molecules combine with vacancies on channel walls within nanochannels, further releasing H_2 or H atoms. In this mechanism, water molecules pass through cracks in the porous outer layer of the corrosion film into regions with higher oxygen vacancy concentrations, enabling further hydrogen diffusion into the metal matrix.

Sankaranarayanan et al. [46] used the CTIP potential model to simulate properties of ultra-thin zirconium oxide films. The CTIP potential model includes a non-electrostatic EAM potential model for metal regions and an electrostatic model for ionic regions [56]. Applied electric fields significantly reduce the activation energy barrier for ion migration through the oxide film, and external electric fields can not only increase oxide film thickness but also reduce differences in oxide stoichiometry at the metal-oxide interface and oxide-gas interface, making the oxide film more uniform. For locally preferentially formed zirconium oxide, Wang et al. [47] found in experimental studies that formation of large-sized zirconium oxide particles occurs not through a growth mechanism but through a coalescence mechanism between small-sized particles. Simulation results showed that if two grains with the same orientation contact each other, dislocations at the grain interface move toward each other and annihilate, merging into a large grain; if orientations differ, new dislocations form at the interface and climb, causing reorientation of one grain before merging into a large grain, but leaving stacking faults and dislocations in the grain.

Zirconium metal has strong hydrogen absorption capacity and may experience hydrogen embrittlement during reactor shutdown. In addition to the diffusion mechanism studies of H atoms in zirconium and zirconium oxide mentioned above, some researchers have studied the effects of hydrogen or hydrides on the mechanical properties of metallic zirconium [57-59], which may be a new approach for experimentally combined MD methods to study zirconium hydrogen embrittlement or fuel-cladding interactions. Although MD methods developed later than experiments, they have demonstrated powerful capabilities in understanding corrosion mechanisms of alloy materials in water-cooled reactors. With future development of interaction potentials for various element-water systems and updates to MD methods, corrosion problems of water-cooled reactor alloy materials (such as pitting, SCC, etc.) will be better understood and predicted.

2.2 Alloy Material Corrosion Simulation in Liquid Metal-Cooled Reactor Environments

Compared with water-cooled reactors, liquid metal-cooled reactors generally have greater nuclear resource utilization and higher thermal efficiency. Liquid metal coolants mainly include sodium, potassium, sodium-potassium alloys, lead, lead-bismuth alloys, lithium, and lead-lithium alloys. Although liquid metals such as sodium and potassium have relatively good compatibility with nuclear reactor structural alloy materials, some liquid metals exhibit strong corrosiveness. Liquid metals primarily corrode through physical dissolution, with the corrosion process mainly involving diffusion phenomena of coolant metal elements. Relevant literature is relatively limited; Table 2 presents recent MD simulation research on alloy material corrosion in liquid metal-cooled reactor environments.

Diffusion coefficient is one of the important physical variables for determining and describing corrosion rates [66]. To clearly understand diffusion-related phenomena, researchers have studied self-diffusion of liquid lead [60, 67] and interdiffusion with stainless steel [18, 68, 69]. These results show that the self-diffusion coefficient of liquid lead follows Arrhenius-type temperature dependence across the temperature range, obtaining activation energy for liquid lead self-diffusion. Over time, the thickness of the filtered mixing layer gradually increases, while the thickness of the interface region depends on temperature—higher temperatures result in larger interface region thickness. During interdiffusion, iron, nickel, and lead atoms interact, and it can be roughly considered that Ni and Fe mainly diffuse in the form of nanoclusters in liquid lead below 1300 K.

Researchers have also studied diffusion properties of lead in droplet states. Zhao et al. [61] used GEAM to investigate wetting characteristics of cylindrical lead droplets on iron surfaces at different temperatures. The service temperature of lead-based reactor structural materials can reach 923 K under normal operating conditions; however, under extreme conditions [70] such as unprotected transient overpower, unprotected loss of flow, and unprotected loss of heat sink, structural material temperatures can reach 923–1073 K. This work considered temperatures for both normal and extreme conditions, with simulation temperatures ranging from 823 to 1123 K (specifically 823, 923, 1023, and 1123 K). The diffusion process of lead droplets can be divided into two stages: momentum-dominated and surface tension-dominated. In the momentum-dominated stage, lead atom velocities in the droplet decrease, while in the surface tension-dominated stage, flow velocities near the liquid-gas interface are significantly higher than in interior regions. As temperature increases, the contact angle between lead droplets and iron surfaces decreases, and liquid lead corrodes the iron matrix. Corrosion degree intensifies with time and temperature, and the team believes that liquid metal diffusion at surface locations follows an interstitial hopping mechanism.

Corrosion degradation of stainless steel by liquid metals mainly results from dissolution of various stainless steel components by liquid metals [71]. Adding corrosion inhibitors can minimize or prevent corrosion. The Indonesian Arkundato team has conducted work on studying corrosion inhibitor effects on solute diffusion behavior in liquid metals.

Arkundato's team used the classical Lennard-Jones potential to simulate lead-bismuth liquid metal systems [72] and studied corrosion inhibition by oxygen [73-75] and nitrogen [76, 77]. The team found that at high temperatures, Pb penetration depth in Fe-10%Ni-16%Cr is deeper than Bi penetration depth, and higher temperatures lead to deeper penetration of both Pb and Bi. Microscopic process analysis revealed that oxygen not only forms iron oxide layers on iron surfaces but also creates a very thin boundary wall separating the iron oxide outer surface from direct interaction with liquid PbBi atoms. However, the corrosion inhibition mechanism of nitrogen atoms is not yet clear.

The Lennard-Jones potential function provides a very poor description of electron motion and cannot well describe reaction processes. To further study liquid metal corrosion behavior, Lei et al. [62] developed an Fe-Pb binary EAM potential, fitting extensive first-principles calculation datasets covering properties of various structures including crystals, non-crystals, surfaces, and solid-liquid interfaces. Compared with ab initio molecular dynamics results and experimental values, their developed Fe-Pb EAM potential can accurately describe ground states, defects, and liquid-phase properties of metal crystals and Fe-Pb solid-liquid interfaces. More importantly, these contents can provide relevant parameters for subsequent development of Fe-Pb-O potentials.

Compared with fission reactors, fusion reactors are considered superior clean energy sources, and liquid lithium is regarded as the preferred material for tritium breeding and cooling in future fusion reactors. However, liquid lithium has stronger wetting and dissolution capabilities for alloys than sodium, even causing selective dissolution of components such as nickel, chromium, and carbon [1]. Additionally, copper alloys are widely used in sealing rings, pipes, and conductors in test systems and are expected to serve as heat sink and structural materials for first walls and divertors in fusion reactors. Therefore, compatibility between liquid lithium and solid copper has received widespread attention.

Xu et al. [63] used MD simulation to study corrosion processes at three different solid-liquid interfaces and investigated interface structure and properties through multiple quantitative characterizations. Results showed that corrosion is anisotropic, related to Cu surface orientation, and that Cu dissolution amount and Li penetration depth both increase with temperature. More importantly, density distribution characterization results showed overlapping density peaks of Li and Cu near the surface, indicating alloying occurs at the surface. This alloy layer retains the original Cu lattice structure and provides certain protective effects. However, when metal surface states are complex, uniform corrosion is often not the main cause of corrosion failure. Therefore, Xu et al. [65] further studied the effect of different grain boundaries on Cu-Li corrosion behavior. Results showed that compatibility tends to decrease as grain boundary energy increases. Additionally, after liquid Li penetration, the potential energy of Cu atoms near grain boundaries increases. Xu et al. believe that liquid metal embrittlement occurs between Cu grain boundaries and liquid Li, which is the direct factor causing polycrystalline Cu fragmentation in liquid Li. Because Cu has low solubility in Li and uniform corrosion forms an alloy layer, physical dissolution corrosion is not the main cause of Cu mass loss. Meng et al. [64] studied corrosion behavior of Cu with grain boundaries and surface mechanical scratches in static liquid Li at 620 K, and these “defect” surface locations were indeed confirmed as breakthrough points for liquid Li penetration into the Cu matrix. When Li atoms that have preferentially penetrated into Cu further diffuse, the originally stable internal metal structure is destroyed, causing bulk Cu on the surface to detach and enter liquid Li, resulting in significant Cu loss. If liquid lithium and copper materials are used simultaneously in future fusion reactors, effective isolation of copper from liquid lithium and application of corrosion-resistant coatings on copper components will be necessary.

Liquid metal coolants operate at high temperatures, and liquid metals exhibit strong diffusion capabilities distinct from solid states. Understanding liquid metal diffusion behavior is a key step in exploring physical dissolution corrosion processes. Additionally, the effects of some corrosion inhibitor substances or impurity components on liquid metal diffusion are not yet clear, and future development of more effective potentials and simulation of multi-component systems will be necessary.

2.3 Alloy Material Corrosion Simulation in Other Environments

In addition to mainstream water-cooled and liquid metal-cooled reactor environments, other environments such as molten salt cooling and supercritical CO_2 (S-CO_2) cooling also present corrosion problems for reactor alloy materials.

For molten salt reactors and integrated fast reactor dry reprocessing being developed in China, corrosion of alloy materials in molten salt environments is particularly important. However, ions in molten states have polarization effects, and the key to corrosion simulation in molten salt environments lies in obtaining interaction potentials that can accurately describe molten salt-metal reactions. Machine learning potentials can, to some extent, break free from physical constraints of materials and may provide new directions for describing such reactions. Currently, Lee et al. [78] have developed a machine learning neural network force field for molten salt LiF-NaF-KF (F-Li-Na-K). The study found that the trained NNFF could reproduce the structure and properties of molten salts with first-principles accuracy and classical molecular dynamics computational efficiency. Additionally, through comparison with rigid ion model (RIM) results, Lee et al. believe that adding anion polarization information in hidden layers is very important. After adding this hidden layer, ion mobility decreased in NNFF. Machine learning potentials have the advantage of continuous training, and this work can provide help for further development of interaction potentials describing molten salt-metal reactions.

Furthermore, the Brayton cycle has attracted attention due to its high efficiency, low cost, and compact system layout, showing good application prospects in nuclear power systems. Corrosion problems between S-CO_2 and iron-based pipelines have also received attention. Currently, simulation work on S-CO_2 corrosion has been initiated, with Yu's team conducting extensive research on corrosion behavior between S-CO_2 and Fe [79-81] using the Aryanpour-2010 reactive force field [35]. The team studied the effect of surface orientation on corrosion rates, believing that atomic arrangement density is the reason why surface orientation affects corrosion reaction rates, and that reactions generally accelerate with increasing temperature. Yang et al. [79] found during simulations that C atoms did not diffuse deeper inward but instead accumulated and became saturated in the surface layer, which may cause the surface layer to become brittle or even spall. Additionally, they found that applied electric fields can inhibit or promote reactions, and that thin oxide film growth can be controlled by adjusting electric field direction and intensity. When the electric field is perpendicular to the solid-liquid interface with the positive direction pointing toward the liquid layer, corrosion reactions are promo

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