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Ab-initio molecular dynamics study of lanthanides in liquid sodium

HIGHLIGHTS

- By using Ab-initio Molecular Dynamics the diffusion coefficients of three lanthanide (Ln) fission products are studied and found to be in the magnitude order of liquid diffusion, which can be applied to validate the “liquid-like” Ln transport mechanism in metallic fuels.
- Structure properties of Na–Ln metallic systems at typical reactor operating temperatures are investigated.
- Ln impurity impacts on electronic density of states on liquid Na are discussed.

ABSTRACT

Keywords:
Ab-initio molecular dynamics
Atomic structure
Electronic density of states
Diffusion coefficient

To mitigate the fuel cladding chemical interaction (FCCI) phenomena in liquid sodium cooled fast reactors, a fundamental understanding of the lanthanide (Ln) transport through liquid Na–Cs filled pores in U–Zr fuel is necessary. In this study, we investigate three abundant Ln fission products diffusion coefficients in liquid Na at multiple temperatures. By utilization of Ab-initio Molecular Dynamics, the Ln diffusivities are found to be in the magnitude order of liquid diffusion (10^{-5} cm^2/s) and the temperature dependence of the diffusivity for different lanthanides in liquid sodium was explored. It is also observed that dilute concentration of Pr and Nd led to a significant change in Na diffusivity. The structural and electronic properties of Na–Ln metallic systems have been investigated. The total coordination number shows dependence on both the temperature and the composition.

1. Introduction

Metallic fuels have shown to be a prospective candidate for next generation fuels due to their relative ease of production and reprocessing, high burnup and inherent recyclability [1]. One of the main concerns with using such fuels is the clad failure due to Fuel Cladding Chemical Interaction (FCCI). As the fuel swells during burnup, the lanthanide (Ln) fission products with particularly abundant cumulative yield can migrate to the fuel periphery and form low-melting point intermetallic compounds with cladding constituents such as Fe and Ni [2]. This chemical interaction between the fission products and the cladding can not only reduce cladding thickness, but also degrade its load-bearing capability [3]. The FCCI phenomenon is deemed as one of the limiting factors of operation of this particular fuel. Therefore, systematic investigations of the Ln redistribution and migration to the fuel surface are essential to understand and mitigate FCCI for optimizing the utilization of metallic fuels.

A “liquid-like” transport mechanism for Ln fission products was recently proposed based on the post irradiation experiment (PIE) from Experimental Breeder Reactor-II (EBR-II) [4]. This model is based on the idea that fission products may transport as solutes in liquid metals such as liquid cesium or cesium-sodium mixture. The mechanism can qualitatively account for the Ln migration to the fuel slug peripheral surface and their deposition with a sludge-like form [4]. To better describe the Ln transport behavior and examine the liquid-like mechanism, the acquisition of fundamental data such as Ln diffusion coefficients in liquid sodium is necessary. Moreover the knowledge of diffusivity in liquid metals is important for prediction of mass transfer rates which plays an important role in several applications such as corrosion [5], phase separation [6], and crystal growth [7]. However, the currently available data from experimental measurements is limited due to the difficulties associated with high temperature experiments and challenge of maintaining the integrity of the samples during the transfer of liquid metals between apparatuses [8]. Therefore, simulation methods provide useful and powerful alternatives to calculate the thermodynamic and transport properties for these systems at elevated temperatures.

In this study the Ab-initio Molecular Dynamics (AIMD) technique is utilized to study the diffusivity of three Ln elements in liquid sodium at multiple characteristic temperatures during reactor operation. In addition, we investigate the effects of Ln impurity atoms on the properties of liquid sodium relevant to their application in nuclear reactors.

2. Computational details

The AIMD simulations were performed by using the Vienna ab initio simulation package (VASP) [9,10]. The projector augmented wave (PAW) method was employed within the density functional theory framework and Perdew-Burke-Ernzerhof (PBE) generalized

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gradient approximation (GGA) was used for the exchange-correlation functional [11]. The first order Methfessel-Paxton's smearing method was used with a width of 0.1 eV to determine the partial occupancies for each wavefunction [12]. The cutoff energy of 400 eV was applied and convergence of energy 10^{-6} eV was set. Spin polarization effects were not considered in this calculation. The Brillouin zone was sampled through the gamma point which is acceptable for large and disordered systems in this case. The AIMD simulations were performed with a time step of 2 fs in the canonical ensemble (NVT) and the Nose-Hoover thermostat was applied with a relaxation time of 20 fs. The systems were initially equilibrated for 5 ps before any statistics of interest were collected for further calculations. The molecular dynamic model of liquid metal was constructed with 128 atoms in the supercell. For binary alloy systems, 4 Ln atoms were introduced in replacement of Na atoms since we only focus on the case with low Ln concentration in the reactor application. Moreover, variation of low Ln concentrations was proved to have negligible effects on the structural or electronic properties in our previous study [13].

3. Results and discussion

3.1. Atomic structure

The structure of the liquid metal is characterized by the form of its pair correlation function (PCF). Fig. 1 shows the calculated total pair correlation functions g(r) of different Na-based metallic systems, which can be obtained by Ref. [14]:

$$g(\mathrm{r}) \approx c_{NaNa}g_{NaNa}(r) + c_{NaLn}g_{NaLn}(r) + c_{LnNa}g_{LnNa}(r) + c_{LnLn}g_{LnLn}(r) \quad (1)$$

where $g_{ij}(r)$ are four partial pair distribution functions of Na–Na, Na–Ln, Ln–Na, Ln–Ln pairs. The weighting factors can be expressed as $x_i x_j Z_i Z_j/(x_{Na}Z_{Na} + x_{Ln}Z_{Ln})^2$ with the atomic number of an atom i, Z_i and the corresponding concentration x_i. In Fig. 1 no well-defined first coordination shell is observed in the $g(r)$ for pure liquid Na, which reflects the deviation from a crystal structure. The liquid binary alloys, Na–Pr and Na–Nd, present a similar shape of PCF as liquid Na and therefore show approximately homogeneous metallic properties. In the Na–Ce binary system, however, segregation phenomena have been observed with the appearance of an extra peak at a distance of around 2.65Å at 723K. As shown in Fig. 2, this peak was found to mainly come from the contribution of the partial pair correlation function, $g_{CeCe}(r)$ with a peak indicating aggregation of the Ce atoms and the Ce separation from the Na solvent atoms. The Na–Ce atomic structure after 60 ps simulation in Fig. 3 shows that all the four Ce atoms gather together during diffusion. This observation, known as segregation, is caused by the rejection of the solutes from a solidified alloy into the liquid phase due to different impurity solubility in liquid and solid phases at the equilibrium temperature. Segregation can be used to predict the

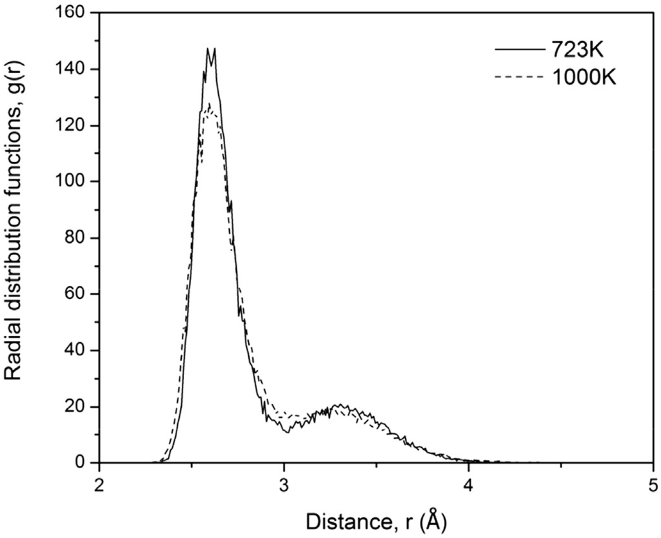

Fig. 2. The Ce–Ce pair correlation functions $g(r)$ at two temperatures.

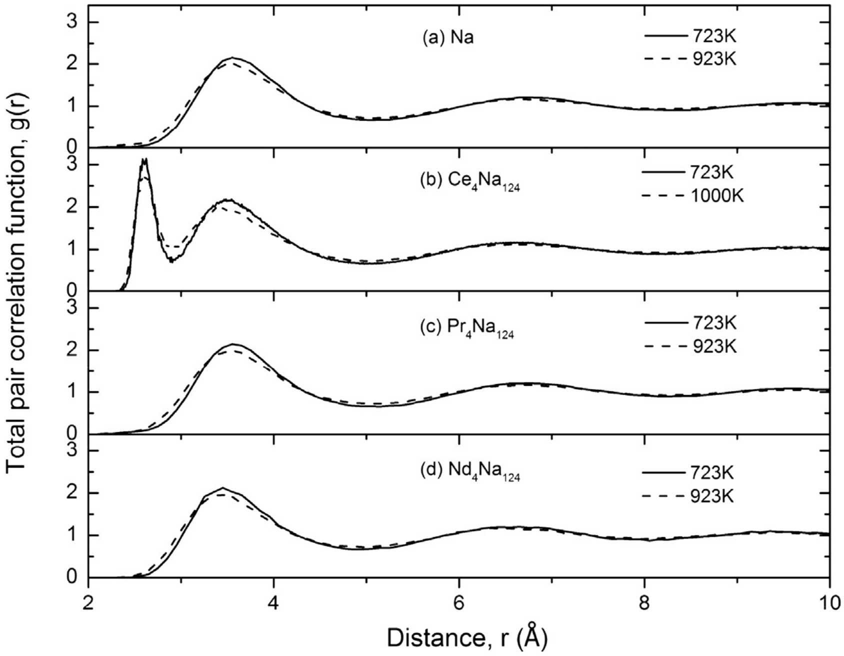

Fig. 1. The total pair correlation functions $g(r)$ of four liquid metallic systems. PCF are calculated at two temperatures for each metallic system.