

博士論文（要約）

論文題目 **STUDY ON MICROSCOPIC
BEHAVIORS OF HYDROGEN ISOTOPE IN
ERBIUM OXIDE FOR TRITIUM PERMEATION
BARRIER**

（トリチウム透過防止用酸化エルビウム中の水素同位体
ミクロ挙動に関する研究）

氏名 毛 偉

In D-T fusion reactors, radioactive tritium must be strictly controlled to establish fuel cycle and radiological safety. It is anticipated that tritium/hydrogen barriers will play a critical role in containing and handling H isotopes within the reactor building and controlling H isotope release to the environment without incurring exorbitant costs. As to coating materials, erbium oxide (Er_2O_3) attracts much attention in the application of tritium permeation barrier (TPB) and is selected as one of the candidate materials for TPB coatings for a fusion blanket system due to high permeation reduction factor (PRF), good compatibility with static and natural convection liquid lithium, high thermodynamics stability at high temperatures and in air, and high electrical resistivity. Hence, more emphasis is now being placed on erbium oxide as candidate materials for TPB coatings in this study.

Up to now, H isotope behaviors in TPB coatings have been studied experimentally in connection with tritium fuel recovery in fusion reactors. Although we have made rapid progress in the fabrication of TPB coatings by different methods such as sputtering deposition and metal-organic decomposition, the surface defects and complex crystal structures still exist in the coatings, which makes it very difficult to elucidate the microscopic behaviors of H isotope in the coatings. Due to its intricate nature, numerous efforts are required to analyze the interaction between H isotope and TPB coatings. Therefore, modeling studies are necessary to conduct experiments efficiently for the universal understanding of (atomic) H isotope process in the H permeation, which is regarded as the rate-determining process with diffusion limited. At present, *ab initio* calculations based on density functional theory (DFT) have become a valuable tool to elucidate the structures and determine the behaviors of interstitial H in metals, alloys, and ceramics. On the other hand, molecular dynamics (MD) simulations are used

to prove the motions of H at elevated temperatures and complement the DFT results in metal oxides. It is, therefore, essential to apply DFT and MD calculations to the behaviors of H in the representative TPB material, Er_2O_3 . In addition, an isotope effect of H behaviors is identified by simulating D/T behaviors in Er_2O_3 using DFT and MD calculations.

The purpose of this study is to investigate the microscopic behaviors of H isotope in Er_2O_3 by computational methods for a fundamental understanding of H isotope permeation through TPB coatings for the D-T fuelling cycle in fusion blanket systems. To realize the microscopic behaviors of H isotope in Er_2O_3 , surface boundary effects, H diffusion in bulk Er_2O_3 with point defects, and H diffusion along Er_2O_3 grain boundaries (GBs) are discussed. The first step is to analyze surface boundary effects on H behaviors by DFT calculations, including surface structural and electronic properties of erbium oxide, H_2 dissociation, H adsorption, and H penetration from the surface to the bulk. It is worth mentioning that cubic Er_2O_3 (001) surface is the most stable surface in the experiments of H isotope (deuterium) permeation at high temperature although phase transition occurs in the permeation. Therefore, more emphasis is being placed on this surface regarding to surface boundary effects. Subsequently, the second step is to investigate the H diffusion in Er_2O_3 with point defects by DFT method, in terms of H diffusivity, H trapping at or near vacancies, and quantum effects on H isotope diffusion. The third step is to study H diffusion along Er_2O_3 GBs by MD simulations, in terms of modeling of GBs, H diffusion in bulk, on surface and along GBs, and GB inclination dependence of H diffusivity. Here, the models of GBs are constructed based on the analysis of electron backscatter diffraction (EBSD), transmission electron microscope (TEM), and X-ray diffraction (XRD) before phase transition from (111) to (001) takes

place in Er_2O_3 . This transition can be attributed to the interaction between atomic H and Er_2O_3 at high temperature (≥ 873 K).

As a result, we identify surface stable adsorption positions on cubic Er_2O_3 surfaces and find that H preferentially adsorbs on top of fourfold-hollow sites on cubic surfaces and transfers electrons to the surfaces, resulting in the formations of covalent bonds to the nearest neighboring four oxygen atoms. Our calculations indicate that the dissociative H atom configurations have adsorption energies that are at least 1.57 eV greater than the H_2 molecule configurations on the surfaces. For our low surface coverage of H (0.89×10^{14} H/cm²), diffusion energy barrier on cubic Er_2O_3 surfaces is predicted to be ~ 0.20 eV, and the penetration energy of at least 1.60 eV is required for the surfaces. Also, the migration barrier for H diffusion between the planes defined by Er_2O_3 units along the favorable $\langle 111 \rangle$ direction is found to be very small at 0.16 eV, while higher migration barriers of 0.41 eV and 1.64 eV are found for the diffusion across the planes, somewhat higher than the diffusion energy barrier of 0.20 eV observed experimentally at 873 K. In addition, interstitial H is predicted to be exothermically trapped when it approaches a vacancy, in which vacancy defect behaves as electron traps since the H-vacancy defect is found to be more stable than the intrinsic vacancy defect. On the other hand, H diffusion in bulk, on (001) surface, and along Σ_{13} (4-3-1)/[111] symmetric tilt grain boundaries (GBs) are evaluated in a temperature range of 673-1073 K, in terms of H diffusivity and H diffusion barriers. It was found that H diffusion is fastest on the free surface, lowest in the bulk, and middle along the GBs. Moreover, the H diffusion data as a function of inclination angles in a series of Σ_3 related GBs has been calculated, with the considerations of H isotope effect. It was found that the local maxima of H diffusion activation energy correspond to two

symmetric tilt GBs, and the asymmetric crystal structures of GBs lead to a decrease of activation energy of H diffusion. H diffusion along GBs indicates that crystal structures play an important role in determining H diffusion barriers and H diffusivity. From the above results, not only are the microscopic behaviors of H isotope well elucidated, but also the mechanism of H isotope diffusion in Er_2O_3 coatings are determined by DFT and MD methods, i.e., H diffusion in Er_2O_3 coatings depends on GBs rather than bulk/lattice due to a higher activation energy found in bulk than along GBs. Also, with a correction of GB density, in which other factors (e.g. H concentration, H diffusion direction) are ignored for H diffusion in Er_2O_3 , the simulated diffusivity along GBs is in good agreement with the experimental data within one order of magnitude. Therefore, we conclude that the approximation of theoretical models used in MD simulations seems reasonable to predict H diffusion in Er_2O_3 coatings on condition that some limiting conditions, such as H concentration, H diffusion direction, vacancy defects, and deviations of the initial configurations in MD simulations, can be neglected regarding to H diffusivity calculations.

Density-functional theory method was used to investigate the fundamental processes of H behaviors at the nanoscale level, with two case studies concerning the surface boundary effects on Er_2O_3 and H diffusion in Er_2O_3 with point defects. H atoms, due to their mobility and small atomic size, are able to form high occupation at crystal defects, but show different interaction with vacancies and GBs. Then, we used the classical MD method to gain an understanding of the dynamic response of erbium oxide to H diffusion migration. This computational work, using DFT and MD techniques, is expected to contribute to the better understanding of H atom process in the H permeation at a fundamental level in order to beneficially complement conventional

laboratory approaches and predict H diffusion phenomena in TPB coatings for the D-T fuelling cycle in fusion blanket systems.