

Tritium Barrier Materials from First Principles Density Functional Theory

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ABSTRACT

The diffusion, permeation and solubility of hydrogen isotopes in metal is of great technological significance as it helps in controlling the hydrogen induced embrittlement and also in the selection of structural materials for reactors with minimum permeability of tritium. Atomistic understanding of the behavior of D/T with metal is highly desirable to design an efficient barrier material. DFT calculations were performed to investigate the interaction and dynamical behaviors of hydrogen isotopes in pure bcc Fe, Cr and W. The adsorption and dissociation pathways for hydrogen isotopes were predicted on (100) surface of Fe, Cr and W. The activation barrier energy for H atom to diffuse from one interstitial void to nearest interstitial void has been computed using nudged elastic band method. The calculated diffusion coefficients, permeability constants and solubility are found to be higher for H compared to its heavier isotopes D and T. Further, the permeability constants predicted to be lowest for W and thus considered as most suitable plasma facing materials.

Keywords: Fe, W, Cr, DFT, Hydrogen isotopes, diffusion, permeation.

Introduction

The heavier deuterium and tritium isotopes of hydrogen have been proposed as the fuels for the first generation of fusion reactors [4]. Tritium like protium easily permeates metallic substance, particularly, under high temperature and reacts vigorously with oxygen. Further, tritium will readily exchange with hydrogen. This is of particular apprehension since tritium poses a severe hazard to living creatures if it exchanges hydrogen in our biological systems due to its radioactive nature. Therefore, it is very imperative to confine tritium within suitable materials and conditions. Polymeric materials are not considered as a choice because of hydrogen-tritium exchange would considerably modify the properties of the polymers. Therefore, a rule of thumb is not to use polymeric substances and instead, attention must be given to either inorganic or metal substances. However, the challenge in the use of metallic containment is that tritium readily permeates them. Therefore, it is of prime necessity to understand the interaction between hydrogen isotopes and metals from atomistic level. In addition, the hydrogen absorption into the bulk of metals is not only important to phenomena such as metal embrittlement but also for hydrogen purification and hydrogen storage. Commonly, steel is

used as containment materials [5,6]. But at high temperatures, hydrogen will diffuse into the steel and may combine with carbon to form cluster of methane at internal voids which at high pressure initiates cracks in the steel and leads to decarburization resulting in to loss of strength and ductility. Steels with 9-12 wt% Cr have received renewed interest in the last years in view of their potential application as structural materials in nuclear reactors and prospective fusion reactors having diffusion coefficients one order of magnitude lower than those of pure Fe metal [7]. The choice of materials for plasma facing components (PFC) in fusion based nuclear power reactor using deuterium-tritium fuel under the highly ambitious project of International Thermo nuclear Experimental Reactor (ITER) is one of the most fascinating and challenging ongoing research activities. The major scientific challenge to achieve the goal is to identify materials which can withstand the extreme heat and particle fluxes from the plasma under incessant neutron bombardment. Large scale computation and experiments are being carried out worldwide on various materials to find out their performance under stringent experimental conditions pertinent to ITER. Further, some metals (mainly steel varieties) are being used as structural material [5,6] or plasma coating substance [8-10] in fusion reactors. Due to its special mechanical and thermal properties, tungsten, W is used in a large number of industrial applications. In view of these properties, W is considered to be the most favored for the highest particle flux due to least erosion and therefore, is anticipated to be used as a divertor plate material in the fusion device of ITER. Additionally, the long time accumulation of high concentration of H can lead to alteration of the material's mechanical and physical properties. Therefore, the knowledge of diffusion behaviour of interstitial H atoms in bulk metals, especially Fe, Cr and W is of utmost necessary which has been studied by a number of authors using density functional theory (DFT) [11-33]. All the calculations infer that the tetrahedral sites in Fe, Cr and W is the most preferable for occupation by interstitial H atoms compared to octahedral sites (o-sites) which is in line with the reported experimental observations [34]. Several computational studies are performed for H diffusion behaviour in Fe and activation energy and pre-factor [11-16] were reported. From computational studies, the reported activation energy was found to be varied from 0.04- 0.09 eV and the values of pre-factor were varied from 10^{-7} – 10^{-8} m²/s. The calculated activation energies for the diffusion of H between two adjacent tetrahedral sites in W were seen to vary widely: 0.20 - 0.38 eV [20, 29-31, 35]. Among these results, activation energy reported by Johnson *et al.* [20] is seen to be agreed well with the experimentally obtained results of Frauenfelder [36, 37], which is the most consistent experimental result to date

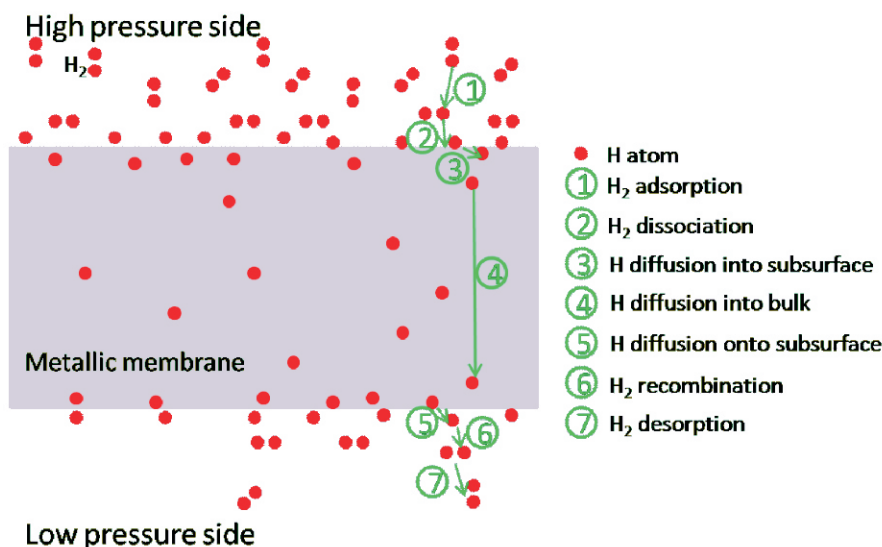


Fig.1: Schematic of Hydrogen isotope permeation through material.

[38]. Although, experimental data on diffusion, permeation and solubility of hydrogen isotopes through tungsten is available for a range of temperature [30, 36, 37, 39-50], no systematic theoretical efforts were put forward to evaluate the permeation and solubility of H isotopes through W. Also, there is a wide variation in the reported experimental data of H isotopes due to challenges associated with permeability measurements [48], particularly for radioactive tritium. Further, the presence of vacancies also play a pivotal role in diffusion behaviour [1, 20, 29, 35]. Hence, the scope of the present article is to fill the existing lacuna by studying the diffusion, permeation and solubility of H isotopes in Fe, Cr and W by DFT calculations.

Computational methods

The generalized gradient approximation (GGA) based Perdew-Burke-Ernzerhof (PBE) density functional [51, 53] using Vienna ab initio Simulation Package [54, 55] was used for all the calculations. The projector augmented wave (PAW) potentials [56, 57] were used to represent the ionic cores. The spin polarization was included for bcc-Fe, Cr and W. The Monkhorst-Pack special k-points [58] was used for integration in the Brillouin zone. During structural relaxation of the supercells, the atomic positions as well as supercell size were relaxed to equilibrium. The forces on all the atoms are kept less than 0.01 eV\AA^{-1} . The phonon calculations are performed using finite displacement method as implemented in the VASP package. The zero point energy ($=1/2 \sum_i \hbar \nu_i$, ν_i is the frequency), ZPE was determined from the H atom frequency by performing phonon calculations by freezing the Fe, Cr and W atoms. Energy cut off and k-point sampling details can be found in the published literature for bcc Fe [1], Cr [2] and W [3]. The standard nudged elastic band (NEB) method [59] is performed to find minimum energy paths and transition states for H atom diffusion.

Results and discussion

In a metallic membrane, H permeation occurs in seven steps (Fig.1): (1) adsorption of H_2 molecule at the high pressure side of the membrane, (2) dissociation of H_2 on the membrane surface, (3) penetration of H from surface to membrane bulk, (4) diffusion of H through the membrane bulk, (5) diffusion of H from membrane bulk to the surface on the collector side of the membrane, (6) recombination of H_2 molecule on the membrane surface, and (7) desorption of H_2 from the collector side surface of the membrane.

Validation of computational methodology

The calculated bond dissociation energy and vibrational frequency of H_2 , D_2 and T_2 molecules are presented in Table 1. The calculated values were found to be in good match with the experimental values [60, 61].

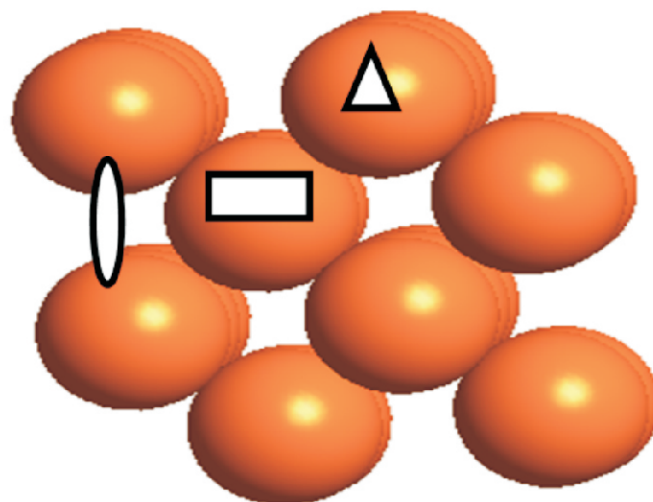


Fig.2: Fe(100) surface: triangle: atop, oval: bridge, rectangle: hollow position.

Table 1. Calculated values of $D_e(\text{eV})$, $\nu(\text{cm}^{-1})$ and ZPE (kJ/mol) for isotopes of H_2 molecule.

Molecule	D_e		ν		ZPE	
	cal	Exp [61]	cal	Exp [60]	cal	Exp [62]
H_2	4.25	4.48	4258	4161	27.78	26.1
D_2	4.33	4.51	3011	2993	19.49	18.5
T_2	4.36		2458		16.40	

Dissociative adsorption of H₂ isotopes on (100) surface of Fe, Cr and W

A dissociative chemisorption of H₂ isotopes can readily take place on metal surface and the corresponding pathway followed by H₂ isotopes dissociation during this process is not fully understood. In the present calculations, we have considered the bridge positions as starting adsorption sites in which H₂ molecule is placed parallel to the surface. In the calculations, H₂ molecule was sequentially moved towards the surface and the positions of atoms were allowed to relax parallel to the surface plane. It was observed that initially the adsorption of H₂ molecule takes place. Further moving down

towards surface leads to dissociation of H₂ molecule in close proximity of the surface. The zero point energy corrected adsorption energies for H₂, D₂ and T₂ with Fe, Cr and W (100) surface are plotted in Fig.3 and variation of H...H distances are presented in Fig. 4. The dissociative adsorption energies of hydrogen isotopes on the (100) surfaces were found to be in the order of $E_{ad}(Fe) < E_{ad}(Cr) < E_{ad}(W)$.

Penetration of H from surface to membrane bulk

After adsorption of H atoms on the surface (S), the next move of H atom will be to migrate to subsurface (T1, T2.. etc), known as absorption. This will continue till it reaches membrane bulk.

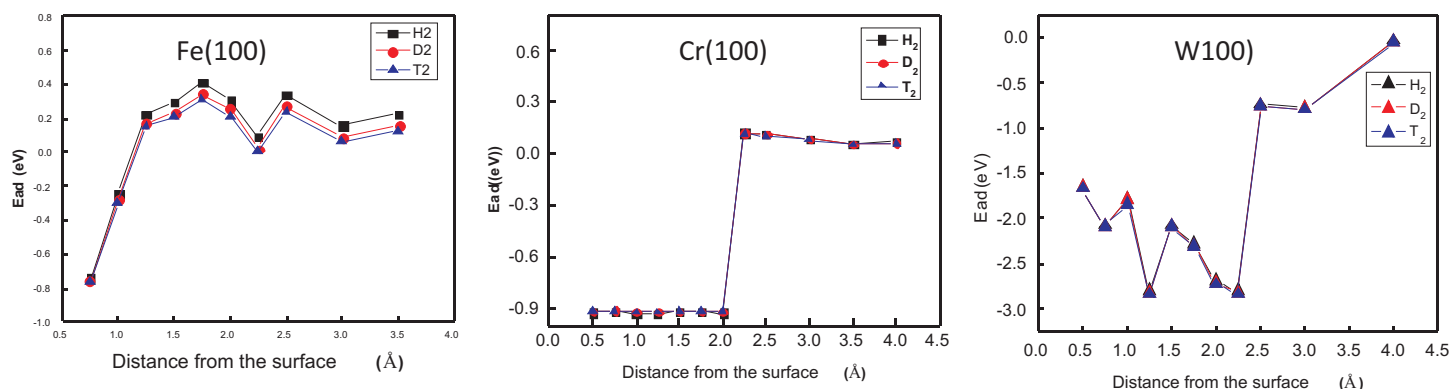


Fig.3: Potential energy surface for dissociative adsorption of H₂ and its isotopic molecules from bridge site to hollow site on (100) surface of Fe, Cr and W as function of the relative distance of H₂ from the surface.

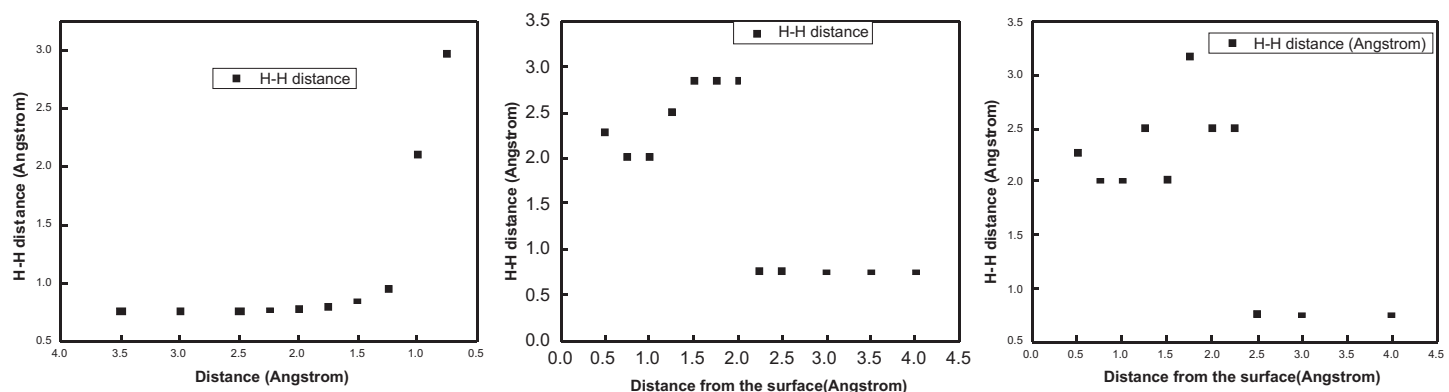


Fig.4: Variations of the H-H bond distances on (100) surface of Fe, Cr and W as function of the relative distance of H₂ molecule from the surface.

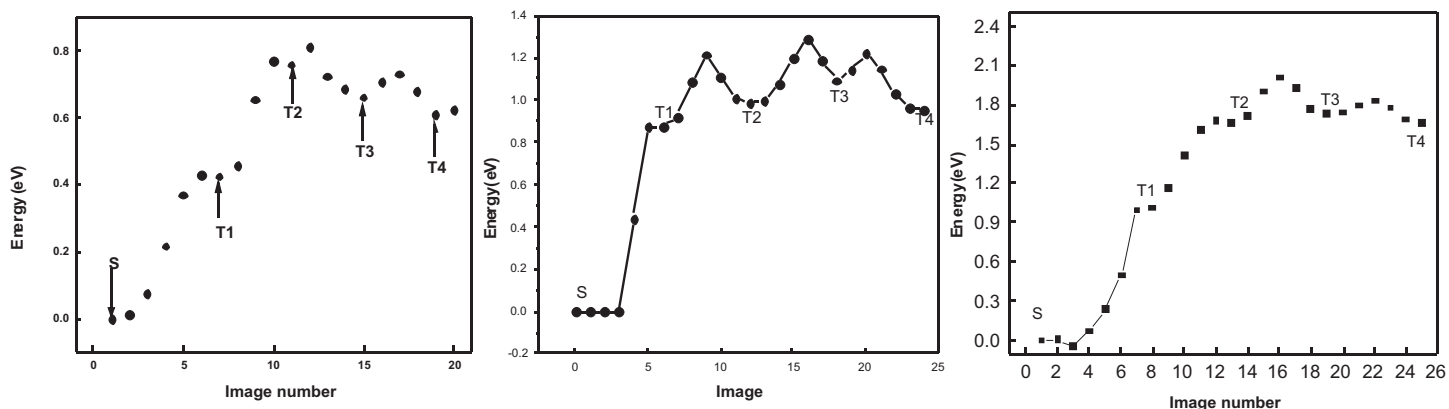


Fig.5: Potential energy surfaces for H diffusion from surface (S) to different sub surface (T1-T4) in Fe, Cr and W(100) surfaces.

NEB calculations were performed for H atom in hollow position(S) on the surface to the tetrahedral site in the various layers of the sub surface (T1, T2, T3 and T4) underneath the surface. Penetration of H from surface to membrane bulk in the case of Fe, Cr and W(100) surfaces were presented in Fig.5. From the calculations it is observed that the penetration H isotopes follows the following trend, $E_{H,D,T}(W_{S-T1}) > E_{H,D,T}(Cr_{S-T1}) > E_{H,D,T}(Fe_{S-T1})$. Further the absorption energies of H isotopes in bulk Fe, Cr and W are calculated and presented in Table 2. From Table 2 it is observed that the H absorption in bulk W is more endothermic than Cr and Fe.

Diffusion of H through the membrane bulk

The diffusion of H and its isotopes is determined using transition-state theory with harmonic approximation[63] and the

random-walk model [64]. The calculated energy barriers for the diffusion of H atom from one T_a site to nearest T_a site in bulk Fe, Cr and W was presented in Fig.6. The activation energy barrier without zero point energy correction was found to be 0.193eV for W [3] which is quite higher compared to pure Fe (0.072 eV) [1] and Cr (0.15eV) [2].

Further, to study the effect of temperature on diffusion, the diffusion constants are evaluated at different temperatures using simple Arrhenius equation. The results are presented in Fig.7. From figure, it is observed that the diffusion coefficients of H, D and T are found to be increased with increase in the temperature in case of Fe, Cr and W. The diffusion coefficients for H in W [3] are lower than for H in Cr [2] and H in Fe[1] and thus might be the reason for considering as plasma facing materials in fusion reactors.

Table 2. Absorption energies (E_{ab}) for hydrogen atoms in bulk Fe, Cr and W.

Bulk	Fe	Cr	W
$M_{16}-H_o$	0.40 (0.44,0.43,0.42)	0.927 (1.008,0.985,0.972)	1.285 (1.400,1.367,1.350)
$M_{16}-H_T$	0.20 (0.29,0.26,0.24)	0.718 (0.847,0.810,0.791)	0.909 (1.030, 0.995, 0.977)
$M_{54}-H_o$	0.43 (0.41,0.42,0.42)	1.040 (1.107,1.088,1.077)	1.156 (1.267, 1.236,1.219)
$M_{54}-H_T$	0.18 (0.29,0.26,0.23)	0.818 (0.945,0.909,0.890)	0.768 (0.887, 0.853, 0.835)

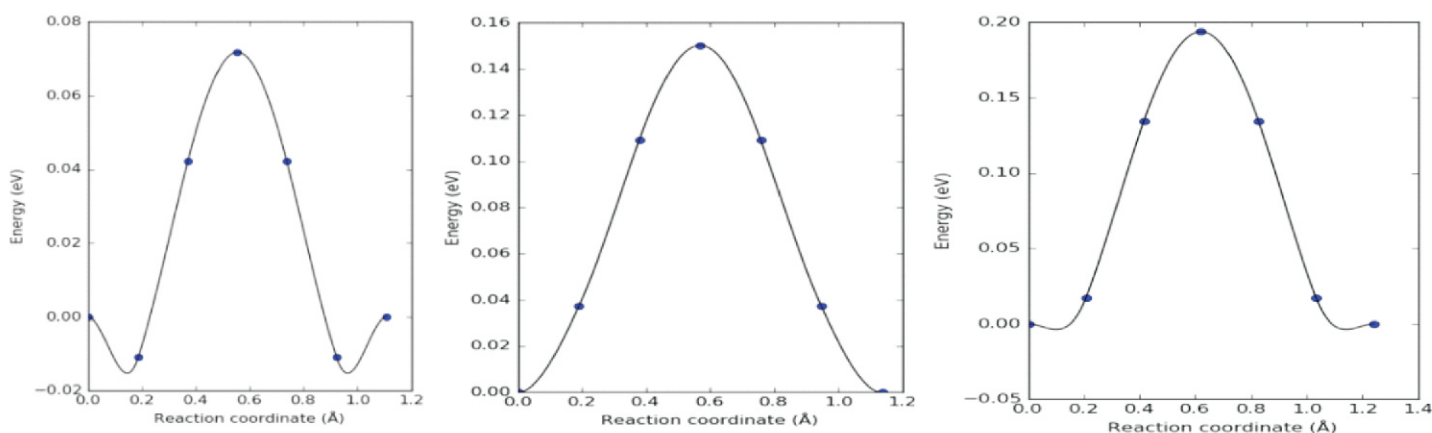


Fig.6: Energy profile for H diffusion from T-T site in bulk Fe , Cr and W.

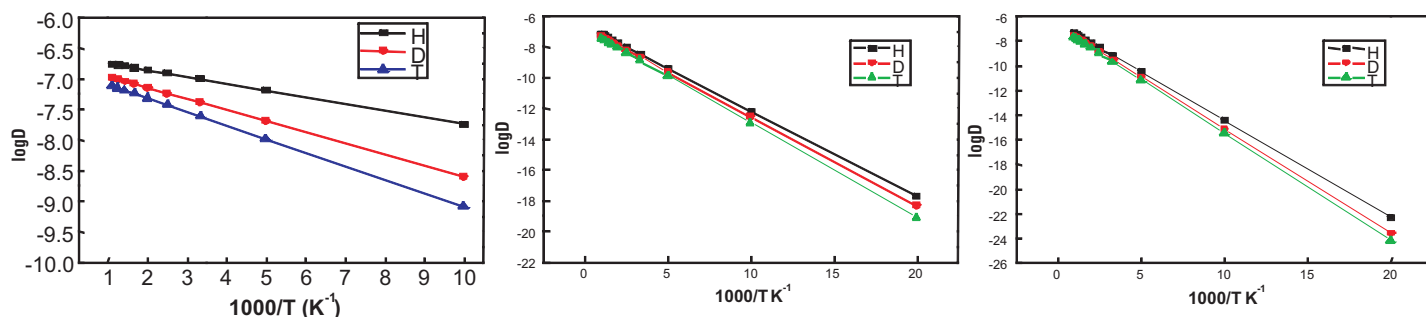


Fig.7: Diffusion coefficients of H, D and T at different temperatures for bulk Fe, Cr and W.

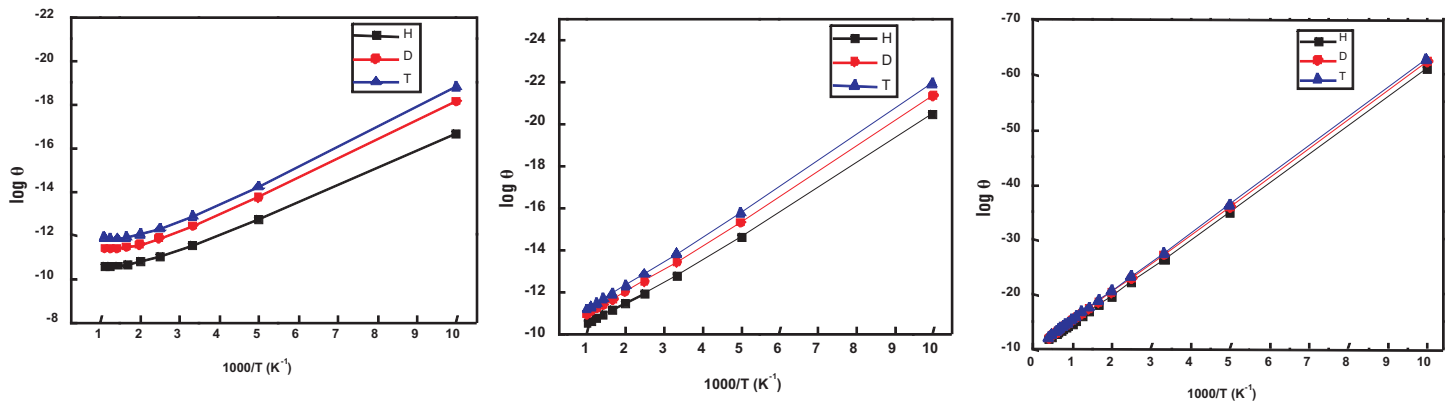


Fig.8: Permeability coefficients of H, D and T at different temperatures for bulk Fe, Cr and W.

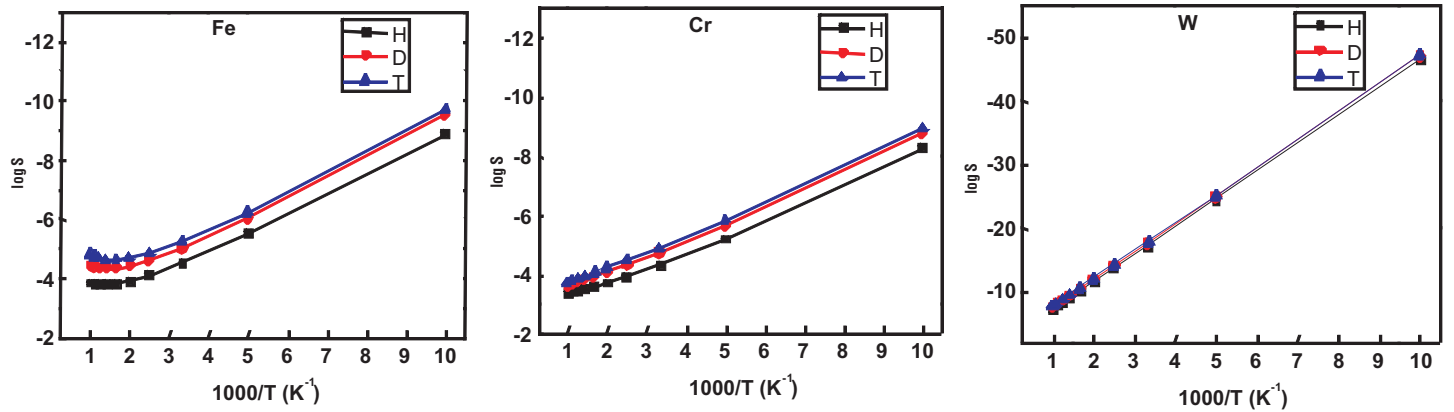


Fig.9: Solubility of H, D and T at different temperatures for bulk Fe, Cr and W.

Permeation and solubility of H₂ isotopes in membrane bulk

The gas permeability (Θ) can be computed using the well known relation [65] as given by the following expression:

$$\Theta = \frac{1}{2} K_s(T) D$$

where $K_s(T)$ is the Sieverts constant represents solubility and D is the diffusion coefficient. The calculated values of Θ for H₂, D₂ and T₂ in Fe, Cr and W at different temperatures are presented in Figure. 8 and respective solubility presented in Figure. 8 and respective solubility S , values are presented in Figure. 9. The permeability coefficients of H₂ is found to be higher compared to its heavier isotopes as expected due to its smaller mass with respect to D and T. Also, the permeation coefficients for H₂ in W [3] are lower than for H₂ in Cr [2] and H₂ in Fe [1]. Further, solubility of H₂ isotopes in Fe, Cr and W followed the similar trend of diffusion and permeation.

Conclusions

DFT calculations were performed to investigate the interaction and dynamical behaviours of hydrogen isotopes in pure bcc Fe, Cr and W. The adsorption and dissociation pathways for hydrogen isotopes were predicted on (100) surface of Fe, Cr and W. The dissociative adsorption energies of hydrogen isotopes on the (100) surfaces were found to be in the order of $E_{ad}(Fe) < E_{ad}(Cr) < E_{ad}(W)$. Further, the penetration of H isotopes follows the trend, $E_{H,D,T}(W_{S-T1}) > E_{H,D,T}(Cr_{S-T1}) > E_{H,D,T}(Fe_{S-T1})$. The activation energy barrier without zero point energy correction was found to be 0.193 eV for W which is quite higher compared to that for pure Fe (0.072 eV) and

Cr (0.150 eV). Thus, the addition of Cr in Fe-Cr alloy helps in reducing permeation of H isotopes. The present observation is in correspondence with the experimentally observed low diffusivity of hydrogen in Fe-Cr steels. The calculated diffusion coefficients, permeability constants and solubility are found to be higher for H compared to its heavier isotopes D and T. The diffusion, permeation and solubility coefficients for H in W are lower than for H in Cr and H in Fe. Further, the calculated diffusion coefficients are shown to be lowest for W and thus might be the basis for considering W as plasma facing materials.

Acknowledgement

Computer Division is acknowledged for providing Anupam super computation facility. Anil Boda and Sk Musharaf Ali acknowledge S. Mukhopadhyay, Head, ChED for encouragement. Work carried out under IAEA Research Agreement No: 24055/RO dated 26th June, 2020.

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References

- [1] A. Boda, S.M. Ali, K.T. Shenoy, S. Mohan, *J. Phys. Chem. C.*, 2019, **123**, 23951-23966.
- [2] A. Boda, S. Bajania, S.M. Ali, K.T. Shenoy, S. Mohan, *J. Nucl. Mater*, 2021, **543**, 152538.

- [3] A. Boda, M.A. Sk, K.T. Shenoy, S. Mohan, *Int. J. Hydrogen Energy*, 2020, **45**, 29095-29109.
- [4] B. Zohuri, Plasma physics and controlled thermonuclear reactions driven fusion energy. Springer, Switzerland, 2016.
- [5] L.M. Germeshuizen, P.W.E. Blom, *Int. J. Hydrogen Energy*, 2013, **38**, 10671-10682.
- [6] A. Zielinski, S. Sobieszczyk, *Int. J. Hydrogen Energy*, 2011 **36**, 8619-8629.
- [7] R.L. Klueh, A.T. Nelson, *J. Nucl. Mater.*, 2007, **371**, 37-52.
- [8] V. Daaz, E. Teliz, F. Ruiz, P.S. Martanez, R. Faccio, F. Zinola, *Int. J. Hydrogen Energy*, 2013, **38**, 12811-12816.
- [9] C. Joseph-Auguste, H. Cheikhvat, N. Djebaili-Chaumeix, E. Deri, *Int. J. Hydrogen Energy*, 2009, **34**, 5970-5975.
- [10] E.S. Solntceva, M.L. Taubin, N.A. Bochkov, V.A. Solntsev, A.A. Yaskolko, *Int. J. Hydrogen Energy*, 2016, **41**, 7206-7212.
- [11] E. Hayward, C.-C. Fu, *Physical Review B - Condensed Matter and Materials Physics*, 2013, **87**, 174103.
- [12] D.E. Jiang, E.A. Carter, *Physical Review B - Condensed Matter and Materials Physics*, 2004, **70**, 064102-1-064102-9.
- [13] J. Sanchez, J. Fulla, C. Andrade, P.L. De Andres, *Physical Review B - Condensed Matter and Materials Physics*, 2008, **78**, 014113.
- [14] D.Di Stefano, M. Mrovec, C. Elsasser, *Physical Review B - Condensed Matter and Materials Physics*, 2015, **92**, 224301.
- [15] D.E. Jiang, E.A. Carter, *Physical Review B - Condensed Matter and Materials Physics*, 2003, **67**, 214103.
- [16] J. Sanchez, J. Fulla, C. Andrade, P.L. de Andres, *Physical Review B*, 2008, **78**, 014113.
- [17] P. Ferrin, S. Kandoi, A.U. Nilekar, M. Mavrikakis, *Surf. Sci.*, 2012, **606**, 679-689.
- [18] C.L. Guerrero, N. Gordillo, R. Iglesias, J.M. Perlado, C. Gonzalez, *Modell. Simul. Mater. Sci. Eng.*, 2016, **24**, 045006.
- [19] K. Heinola, T. Ahlgren, *Phys. Rev. B*, 2010, **81**, 073409.
- [20] D.F. Johnson, E.A. Carter, *J. Mater. Res.*, 2010, **25**, 315-327.
- [21] K. Kwak, M. Chou, N. Troullier, *Phys. Rev. B*, 1996, **53**, 13734-13739.
- [22] G.H. Lu, H.B. Zhou, C.S. Becquart, *Nucl. Fusion*, 2014, **54**, 086001.
- [23] A. Moitra, K. Solanki, *Comput. Mater. Sci.*, 2011, **50**, 2291-2294.
- [24] A. Nojima, K. Yamashita, *Surf. Sci.*, 2007, **601**, 3003-3011.
- [25] Z.A. Piazza, M. Ajmalghan, Y. Ferro, R.D. Kolasinski, *Acta Mater*, 2018, **145**, 388-398.
- [26] L. Sun, S. Jin, G.H. Lu, L. Wang, *Scripta Mater*, 2016, **122**, 14-17.
- [27] L. Sun, Y.-N. Liu, W. Xiao, M. Zhou, *Mater. Today. Comm.*, **17**, 2018, 511-516.
- [28] J. Wang, Y. Zhang, H.B. Zhou, S. Jin, G.H. Lu, *J. Nucl. Mater*, 2015 **461**, 230-235.
- [29] N. Fernandez, Y. Ferro, D. Kato, *Acta Mater*, 2015, **94**, 307-318.
- [30] K. Heinola, T. Ahlgren, *J. Appl. Phys.*, 2010, **107**, 113531.
- [31] J. Xu, J. Zhao, *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms*, 2009, **267**, 3170-3174.
- [32] E.D.V. Gómez, S. Amaya-Roncancio, L.B. Avalué, D.H. Linares, M.C. Gimenez, *Appl. Surf. Sci.*, 2017, **420**, 1-8.
- [33] L. Zhang, L. Qiao, T. Bligaard, Y. Su, *Appl. Surf. Sci.* **457** (2018) 280-286.
- [34] S.T. Picraux, F.L. Vook, *Phys. Rev. Lett.*, 1974 **33** 1216-1220.
- [35] Y.L. Liu, Y. Zhang, G.N. Luo, G.H. Lu, *J. Nucl. Mater*, 2009, **390-391**, 1032-1034.
- [36] R. Frauenfelder, *J. Vac. Sci. Technol.*, 1969, **6**, 388-397.
- [37] R. Frauenfelder, *J. Chem. Phys.*, 1968, **48**, 3955-3965.
- [38] T. Tanabe, *Phys. Scr. T*, 2014, **159**, 014044.
- [39] E.A. Aitken, H.C. Brassfield, P.K. Conn, E.C. Duderstadt, R.E. Fryxell, *Trans. Met. Soc. AIME*, 1967, **239**, 1565.
- [40] G. Benamati, E. Serra, C.H. Wu, *J. Nucl. Mater*, 2000, **283-287**, 1033-1037.
- [41] D.A. Buchenauer, R.A. Karnesky, Z.Z. Fang, C. Ren, Y. Oya, T. Otsuka, Y. Yamauchi, J.A. Whaley, *Fusion Eng. Des.*, 2016, **109-111**, 104-108.
- [42] G.A. Esteban, A. Perujo, L.A. Sedano, K. Douglas, *J. Nucl. Mater*, 2001, **295**, 49-56.
- [43] T. Ikeda, T. Otsuka, T. Tanabe, *J. Nucl. Mater*, 2011, **415**, S684-S687.
- [44] T. Ikeda, T. Otsuka, T. Tanabe, *Fusion Sci. Technol.*, 2011, **60**, 1463-1466.
- [45] H. Nakamura, W. Shu, T. Hayashi, M. Nishi, *J. Nucl. Mater*, 2003, **313-316**, 679-684.
- [46] T. Oda, *Fusion Eng. Des.*, 2016 **112**, 102-116.
- [47] T. Otsuka, T. Hoshihira, T. Tanabe, *Physica Scripta*, 2009, **TT138**, 14052.
- [48] M. Shimada, R.J. Pawelko, *Fusion Eng. Des.*, 2019, **146**, 1988-1992.
- [49] A.P. Zakharov, V.M. Sharapov, E.I. Evko, *Soviet Mater. Sci.*, 1975, **9**, 149-153.

- [50] W.J. Arnoult, R.B. McLellan, *Acta Metall*, 1973, **21**, 1397-1403.
- [51] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
- [52] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, **80**, 1998, 891.
- [53] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, *Phys. Rev. B*, 1992, **46**, 6671-6687.
- [54] G. Kresse, J. Furthmuller, *Phys. Rev. B*, 1996, **54**, 11169-11186.
- [55] G. Kresse, J. Hafner, *Phys. Rev. B*, 1993, **47**, 558-561.
- [56] P.E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953-17979.
- [57] G. Kresse, *Phys. Rev. B*, 1999, **59**, 1758-1775.
- [58] H.J. Monkhorst, J.D. Pack, *Phys. Rev. B*, 1976, **13**, 5188-5192.
- [59] H. Jansson, G. Mills, K.W. Jacobsen, *Classical and Quantum Dynamics in Condensed Phase Simulations*, *WORLD SCIENTIFIC*, 1998, p. 385-404.
- [60] B.P. Stoicheff, *Canadian Journal of Physics*, 1957, **35**, 730-741.
- [61] D. Sprecher, C. Jungen, W. Ubachs, F. Merkt, *Faraday Discussions*, 2011, **150**, 51-70.
- [62] K.K. Irikura, *Journal of Physical and Chemical Reference Data*, 2007, **36**, 389-397.
- [63] G.H. Vineyard, *Journal of Physics and Chemistry of Solids*, 1957, **3**, 121-127.
- [64] C. Wert, C. Zener, *Physical Review*, 1949, **76**, 1169-1175.
- [65] B.D. Morreale, M.V. Ciocco, R.M. Enick, B.I. Morsi, B.H. Howard, A.V. Cugini, K.S. Rothenberger, *J. Membr. Sci.*, 2003, **212**, 87-97.