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Damage accumulation under low energy hydrogen ion irradiation

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Abstract

In order to understand the characteristic defect clustering processes under hydrogen ion irradiation with fusion relevant energy and the underlining defect interactions controlling the processes, accumulation of defects and defect–hydrogen complexes are calculated numerically using the homogeneous reaction kinetics and rate equations. These calculations do not consider the nucleation and growth of hydrogen bubbles. The present calculations yield a very high concentration (order of 10^{-2}) of vacancy–hydrogen (VH) complexes and a high growth rate and relatively low concentration of interstitial loops (IL). These results are in disagreement with the experimental results. Within the framework of the present calculations, the experimental results could be explained, however, by postulating very low reaction efficiencies of interstitials with VH complexes and interstitial loops. The validity of these postulates and impacts of the simplified assumptions are discussed.

1. Introduction

Plasma facing components of fusion devices will be heavily bombarded with ions or neutrals of hydrogen isotopes with energies ranging from a few 10 eV to a few keV. The hydrogen particles above several 100 eV cause not only sputtering but also displacement damage in the sub-surface region. A special feature of the damage by these particles is that the number of the injected hydrogen atoms is comparable with that of displaced atoms. One may expect that the high concentration of hydrogen atoms would modify the microstructural evolution by interacting with the radiation induced defects and among themselves.

Irradiation experiments with keV range energy have been carried out for many metals such as Mo [1,2], W [3], Ni [4] and Cu [5] and the results have revealed that the damage evolutions are very different from those formed in the corresponding experiments with electrons. The nucleation of interstitial loops, for example, lasted longer and the loop density saturated at a level more than one order of magnitude higher than that observed during electron irradiation with a similar damage rate. It was also reported that at a constant damage rate the interstitial loops grew linearly in size [2]. These results implied that the concentration of interstitials remained almost constant during long irradiation. In order to understand the mechanism of these defect clustering processes under the low energy hydrogen ion irradiation, numerical calculations for low dose have been carried out and the results are described and discussed in the present paper.

2. Clustering of defects and hydrogen atoms

Hydrogen ions at energies in the keV range injected into materials cause displacement damage by colliding with lattice atoms and are gradually thermalized by repeating the collisions. Fig. 1 shows depth distributions of the displacement damage and the thermalized hydrogen atoms for 8 keV-hydrogen ion irradiation. The special features of keV-energy hydrogen ion irradiation is that the damage and the hydrogen atoms are localized in the sub-surface region at a depth of several 10 nm and damage rate and hydrogen deposition rate are comparable. These features indicate that hydrogen–defect interactions and localization of damage may play important role in the damage accumulation under the hydrogen ion irradiation. In the present work, estimates are made of clustering of hydrogen and irradiation-induced defects within the framework of homo-

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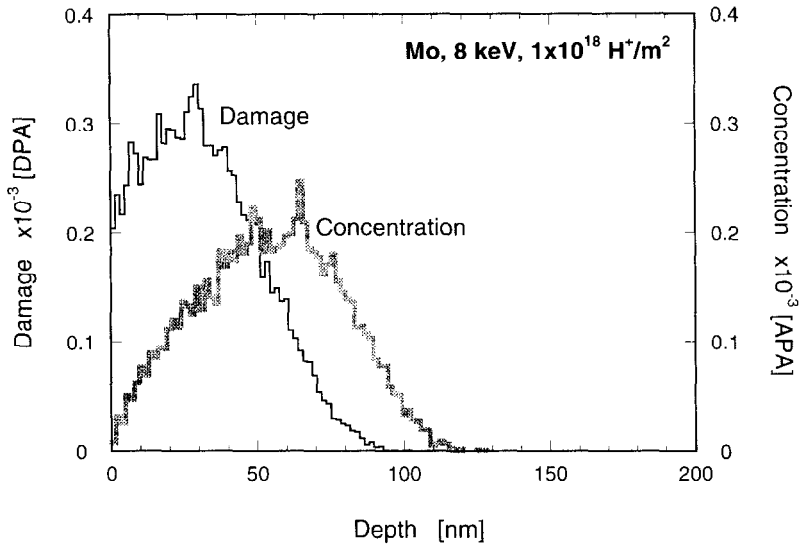

Fig. 1. Depth distributions of damage and injected hydrogen atoms in Mo energy and fluence of hydrogen ion are 8 keV and 1×10^{18} ions/m^2, respectively.

geneous reaction kinetics and the mean-field theory using the following assumptions.

(1) The production rate of vacancies (V) and interstitials (I), denoted as P, and the deposition rate of hydrogen atoms (H), denoted as P_H, are estimated as a function of depth (x) by using the TRIM-code [6].

(2) Specimen thickness is assumed to be 200 nm to match the irradiation experiments under TEM observation [2]. Specimen surfaces are assumed to be perfect sinks for defects and hydrogen. Internal sinks (S) such as impurity atoms are also introduced.

(3) I, V and H are assumed to be mobile and bring about defect reactions. The migration energy of I, V and H are taken from the literature; $E_I^M = 0.083$ eV [7], $E_V^M = 1.3$ eV [8] and $E_H^M = 0.1$ eV [9] and the corresponding mobilities are given by $M_I = \nu_I \exp(-E_I^M/kT)$, $M_V = \nu_V \exp(-E_V^M/kT)$ and $M_H = \nu_H \exp(-E_H^M/kT)$, respectively. Here T denotes temperature and ν_I and ν_H denote jump frequencies of an interstitial and a hydrogen atom and are assumed to be 10^{13} jumps/s.

(4) Di-interstitials (2I) are immobile and thermally stable. This means that 2I are the nucleus of interstitial loops.

(5) Impurity–hydrogen complexes (SH) and interstitial loops (IL) are also immobile and thermally stable.

(6) One hydrogen atom can be trapped in a vacancy and form a V–H complex (VH). VH can dissociate thermally or by absorbing I. The thermal dissociation rate of VH denoted as M_B is given by $M_B = \nu_{VH} \exp[-(E_H^M + E_{VH}^B)/kT]$. Due to the lack of definite data, ν_{VH} is assumed to be 10^{11} jumps/s and E_{VH}^B is used as a fitting parameter in the calculations. The formation of larger complexes (mV–nH) ($m = 1$, $n \geq 2$ and $m \geq 2$, $n \geq 1$, number of vacancies and trapped hydrogen atoms), is neglected to simplify the reaction equations.

(7) The formation of vacancy clusters (mV) is also neglected.

Within the framework of the defect reaction model described above, the variation of interstitial concentration, C_I, vacancy concentration, C_V, and hydrogen concentration, C_H, under steady hydrogen ion irradiation can be described by the following equations.

(a) Production of interstitials:

$$\begin{aligned} dC_I/dt &= P(1-C_V)(1-Z_{IV}C_V) \\ &\quad - \underbrace{Z_{IV}(M_I+M_V)C_IC_V}_{\text{(recombination of I and V)}} - \underbrace{Z_{SI}M_IC_{SI}C_I}_{\text{(flow of V to permanent sink)}} \\ &\quad - \underbrace{Z_{LI}M_I(C_{LI}C_L)^{1/2}C_I}_{\text{(flow of I to I-loop)}} - \underbrace{Z_{IVH}M_IC_IC_{VH}}_{\text{(I–VH combination)}} \\ &\quad - \underbrace{2Z_{II}M_IC_IC_I}_{\text{(I–I combination)}} + \underbrace{D_I(d^2C_I/dx^2)}_{\text{(diffusion of I)}}. \end{aligned} \quad (1)$$

(b) Production of vacancies:

$$\begin{aligned} dC_V/dt &= P(1-C_V)(1-Z_{IV}C_V) \\ &\quad - \underbrace{Z_{IV}(M_I+M_V)C_IC_V}_{\text{(dissociation recombination I–V)}} \\ &\quad - \underbrace{Z_{SV}M_VC_{SV}C_V}_{\text{(flow of V to permanent sinks)}} - \underbrace{Z_{LV}M_V(C_{LI}C_L)^{1/2}C_V}_{\text{(flow of V to I-loop)}} \\ &\quad - \underbrace{Z_{VH}(M_V+M_H)C_VC_H}_{\text{(recombination of V–H)}} + \underbrace{Z_{VHD}M_BC_{VH}}_{\text{(dissociation of VH)}} \\ &\quad + \underbrace{D_V(d^2C_V/dx^2)}_{\text{(diffusion of V)}}. \end{aligned} \quad (2)$$

(c) Production of hydrogen atoms:

$$\begin{aligned} dC_H/dt &= P_H - \underset{\text{(combination of V–H)}}{Z_{VH}(M_V + M_H)C_V C_H} \\ &+ \underset{\text{(combination of I–VH)}}{Z_{IVH} M_I C_I C_{VH}} + \underset{\text{(dissociation of VH)}}{Z_{VHD} M_B C_{VH}} \\ &- \underset{\text{(flow of H to permanent sink)}}{Z_{SH} M_H C_S C_H} + \underset{\text{(dissociation of H from sink)}}{Z_{SHD} M_{SB} C_{SH}} \\ &+ \underset{\text{(diffusion of H)}}{D_H\left(d^2 C_H/dx^2\right)}. \end{aligned} \tag{3}$$

D_I, D_V and D_H denote diffusivity of I, V and H, respectively. The meaning of each term is denoted below it. Z_{ij}s denote reaction site number of defect i and defect j. The term of flow of I to I-loops in Eqs. (1) and (2) is given by $Z_{LI} M_I (C_{LI}/C_L)^{1/2} C_L C_I$ [10].

Assuming that 2I is the nucleus of IL, the variation of interstitial loop concentration (C_L) and concentration of interstitials absorbed into interstitial loops (C_{LI}) can be approximated by

$$\frac{dC_L}{dt} = \frac{dC_{2I}}{dt} = (Z_{II} M_I C_I - Z_{IV} M_V C_V) C_I \tag{4}$$

and

$$\begin{aligned} dC_L/dt &= \underset{\text{(flow of I to I-loops)}}{Z_{LI} M_I (C_{LI} C_L)^{1/2} C_I} \\ &- \underset{\text{(flow of V to I-loops)}}{Z_{LV} M_V (C_{LI} C_L)^{1/2} C_V} + \underset{\text{(combination of I–I)}}{2 Z_{II} M_I C_I C_I}, \end{aligned} \tag{5}$$

respectively.

On the other hand, variations of the concentration of VH, impurity (S) and SH are given by the following rate equations, respectively:

$$\begin{aligned} dC_{VH}/dt &= \underset{\text{(combination of V–H)}}{Z_{VH}(M_V + M_H)C_V C_H} \\ &- \underset{\text{(combination of I–VH)}}{Z_{IVH} M_I C_I C_{VH}} - \underset{\text{(dissociation of VH)}}{Z_{VHD} M_B C_{VH}}, \end{aligned} \tag{6}$$

$$dC_S/dt = \underset{\text{(flow of H to sink)}}{- Z_{SH} M_H C_S C_H} + \underset{\text{(dissociation of H from sink)}}{Z_{SHD} M_{SB} C_{SH}}, \tag{7}$$

$$dC_{SH}/dt = \underset{\text{(flow of H to sink)}}{Z_{SH} M_H C_S C_H} - \underset{\text{(dissociation of H from sink)}}{Z_{SHD} M_{SB} C_{SH}}. \tag{8}$$

3. Numerical calculations

During the hydrogen ion irradiation of Mo at room temperature (8 keV, 2×10^{18} ions/m^{2}s) [2], the concentration of interstitial loops increased gradually and reached a value of about 5×10^{-7} in 100 s. The interstitial loops grew linearly with irradiation time and their typical size at 100 s was 4 nm. This means that about 200 interstitials were absorbed in a loop in 100 s of irradiation. Keeping these results in mind, we examined the influences of (1) the interaction between VH and I, (2) the absorption efficiency of I to IL and (3) the binding energy of VH by changing Z_{IVH}, Z_{LI} and E^B_{VH} as fitting parameters. The values of Z_{ij}, with the exception of Z_{IVH} and Z_{LI}, are assumed to correspond to the spontaneous recombination at the first or second nearest positions.

3.1. Effect of VH–I interaction

The VH–I interaction plays an essential role for the accumulation of I and V. Namely, if the VH–I reaction is unfavorable ($Z_{IVH} \ll 1$), vacancies lose their role as sinks for interstitials by trapping a hydrogen atom in it. If this reaction is favorable, V and I annihilate mutually by emitting the trapped hydrogen atom into the lattice. Fig. 2 shows the accumulation of defects at room temperature at the depth of the damage peak (30 nm) for $Z_{IVH} = 1$ and $Z_{IVH} = 0$. Major parameters used in the calculation are listed in Fig. 2. In these calculations VH can hardly dissociate thermally due to a rather high V–H binding energy E^B_{VH} (= 0.8 eV). Because of the high migration efficiency of hydrogen atoms ($C_H M_H$) radiation induced V, which is thermally immobile at room temperature due to high migration energy (1.3 eV), is occupied by a hydrogen atom in a very short time (about $1/Z_{VH} M_H C_H \fallingdotseq 10^{-3}$ s).

If E^B_{VH} is high enough, VH become major defects at a high dose. C_V, on the other hand, stays at a constant level by the balance of the production term P and the V–H formation term.

In the case of $Z_{IVH} = 1$, VH act as a good sink for I and, therefore, C_I decreases with increasing C_{VH} above 10^{-1} s. Due to the reduction of C_I ($\propto t^{-1/2}$), interstitial loops grow with $t^{1/2}$ and C_L saturates at low level (about 5×10^{-9}). These results do not agree with the experimental results. In the case of $Z_{IVH} = 0$, on the other hand, VH does not act as a sink for I but major sinks for I are free vacancies and the surfaces. Because both of these types of sinks are time-independent, C_I is almost constant up to 10 s. It seems that the very weak reaction of I and VH is essential for keeping C_I at a constant level. Due to the fast growth of IL (about 10^5 interstitials/loop in 100 s), IL becomes a major sink for I and consequently the level of C_I goes down during irradiation beyond 10 s. In order to fit the experimental data of the loop size, C_{IL}/C_L should be about 200 in 100 s. We need further adjustment of parameters to suppress the growth of interstitial loops.

3.2. Effects of I–IL interaction

Because the loop growth is directly related to the reaction coefficient of I–IL, we tried to adjust Z_{LI} to

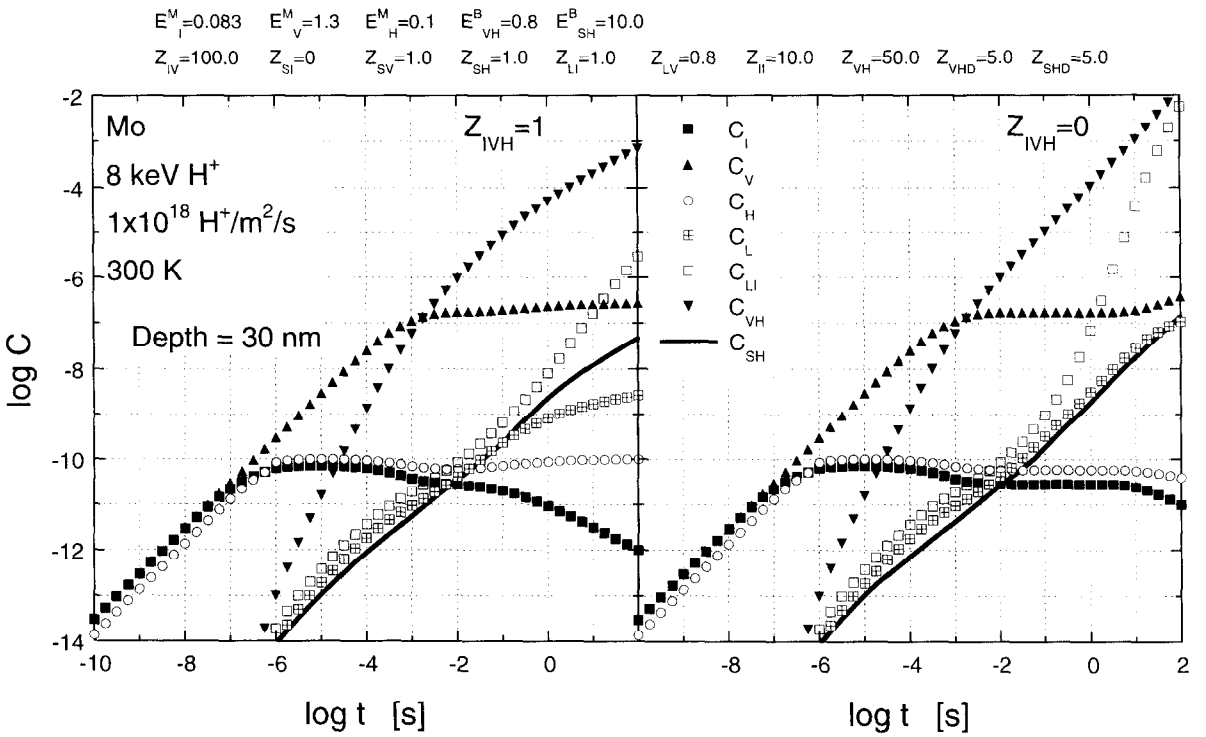

Fig. 2. Z_{IVH} dependence of defect accumulation. By reducing Z_{IVH}, C_I-constant region expands.

obtain the experimentally observed loop size. Fig. 3 shows the accumulation of defects for $Z_{LI} = 0.02$, 0.1 and 1. With decreasing Z_{LI}, the duration of the C_I constant state increases and the size of IL decreases. In order to explain the experimentally observed density, the size and linear growth of interstitial loops Z_{LI} should be about 0.02. In a simple damage case such as fast electron irradiation, where only V and I are produced, Z_{LI}/g means the spontaneous reaction site number of I–IL absorption process per one atomic site along a dislocation loop and is the order of 1 to

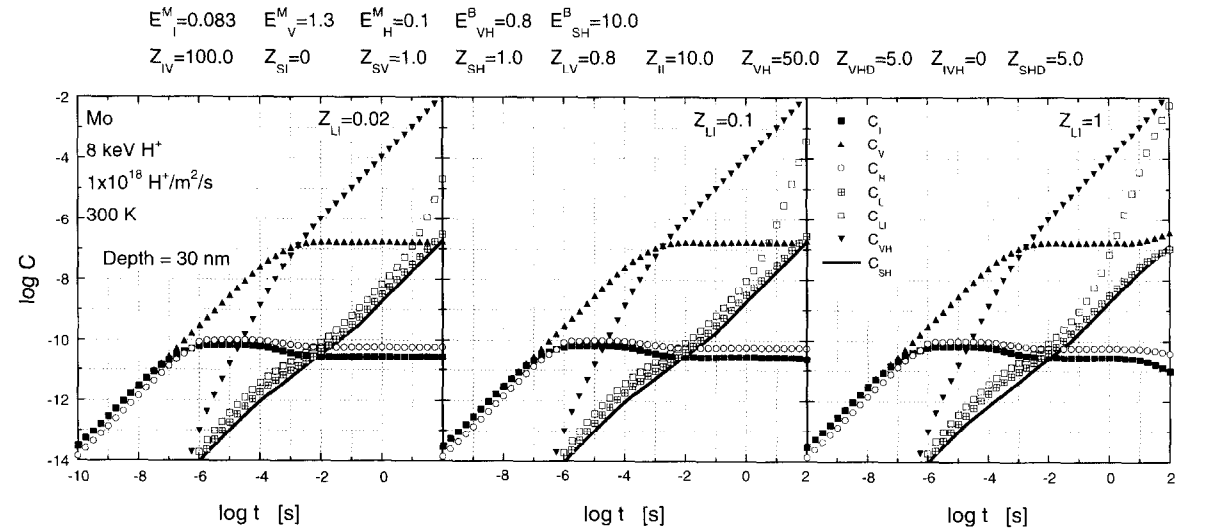

Fig. 3. Z_{LI} dependence of defect accumulation. In order to explain the experimentally observed loop size and linear growth, Z_{LI} should be around 0.02.

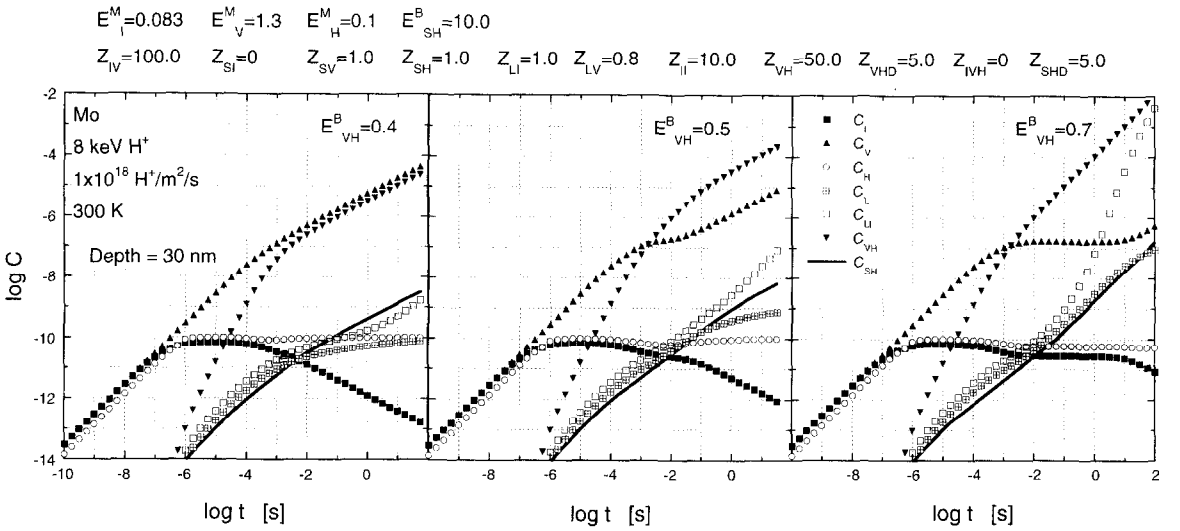

Fig. 4. E^{B}_{VH} dependence of defect accumulation. For lower binding energy, C_I decreases with irradiation time, because of increasing C_V.

10. Here, g is the geometrical parameter depending on the shape of the loop and about 3.5 for a circular shape. Z_{LI}/g smaller than 1 indicates that repulsive interaction or a barrier exists for the I–IL absorption process. A possible explanation is the effect of trapped hydrogen atoms at the dislocation core. Because of the high migration efficiency of hydrogen atoms and the high binding energy, it is expected that hydrogen atoms occupy the dislocation core and reduce the long range elastic interaction between free interstitials and the dislocation loop. It is even possible that the trapped hydrogen atoms may prevent the absorption of interstitials.

3.3. Effects of V–H binding

In the numerical calculations discussed so far rather high V–H binding energy is assumed. TDS experiments [11] indicated that strong trapping sites for a hydrogen atom in Mo at room temperature were impurity atoms, dislocation loops and bubbles. Hydrogen atoms trapped in single vacancies during irradiation were detrapped by holding at room temperature for a few hours. This indicates that the dissociation rate of VH at room temperature should be higher than 10^{-3} jump/s. An E^{B}_{VH} of 0.7 eV or less ($E^{V}_{H} = 0.1$ eV, $\nu_{VH} = 10^{11}$ jumps/s) satisfies this

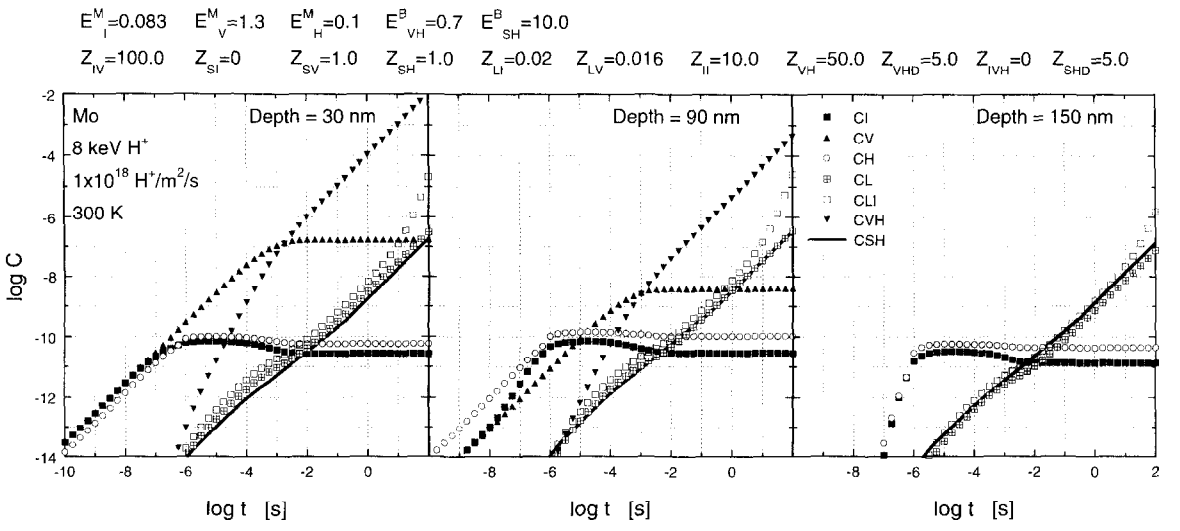

Fig. 5. Defect accumulation at the depth of 30, 90 and 150 nm for the best fitting case. Interstitial loops and SH complexes are formed by the diffusion of interstitials and hydrogen atoms even at the depth of 150 nm, where no primary damage occur.

condition. Fig. 4 shows the accumulation of defects for $E^B_{VH} = 0.4$, 0.5 and 0.7 eV and the corresponding thermal dissociation rates, M_B, are 3.9×10^2/s, 8.3/s and 3.6×10^{-3}/s, respectively. In the case of 0.4 and 0.5 eV, the C_I constant state does not continue long, because C_V increases due to active thermal dissociation of VH. The duration time of the C_V constant state increases with increasing E^B_{VH}. When the irradiation time exceeds the life of VH given by $1/M_B$, C_V starts to increase again and leads the reduction in C_I. In order to explain the experimentally observed long linear growth of IL, we should assume an E^B_{VH} of about 0.7 eV for $\nu_{VH} = 10^{11}$ jumps/s. Though we cannot discuss the binding energy in detail due to the lack of experimental data changing irradiation temperature, the present value is close to the theoretically estimated value of 0.6 eV [12].

To simplify the rate equations in the present model it is assumed that single vacancies can trap only a single hydrogen atom. If we allow the trapping of a hydrogen molecule (V2H), which must have a higher trapping energy than hydrogen atoms, V2H complexes act as a 'free vacancy killer' just as VH in the present simple case, even if the E^B_{VH} is rather low. Though it is difficult to discuss the details of V–H interaction due to the limitation of the present rather simplified model, we can almost explain the experimental results by assuming 0.7 eV to be the effective trapping energy of the V–H complex.

Based on the discussion described above, we can get a very good fitting by assuming the following parameters:

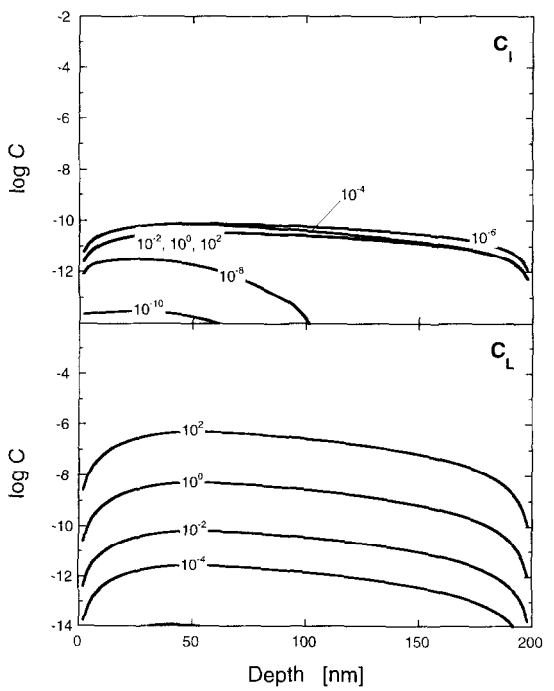

Fig. 6. Depth distributions of C_I and C_L.

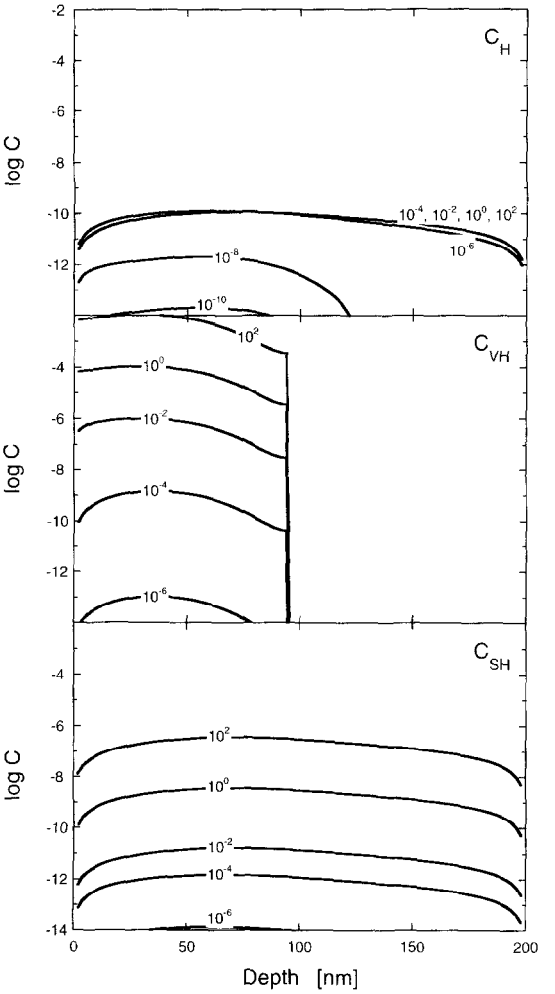

Fig. 7. Depth distributions of C_H, C_{HV} and C_{SH}.

$Z_{IVH} = 0$, $Z_{LI} = 0.02$ and $E^B_{VH} = 0.7$ eV ($\nu_{VH} = 10^{11}$ jumps/s). Fig. 5 shows the time evolution of defect concentrations at several different depths under 8 keV-hydrogen ion irradiation at room temperature; loop concentration remains at a constant level and the average number of interstitials in each loop given by C_{IL}/C_L is about 100 at the damage peak.

3.4. Depth distribution of defects

Fig. 6 shows the depth distribution of C_I and C_L for the best fitting case. The numbers in Fig. 6 denote the irradiation time in seconds. Due to its high mobility, I diffuses immediately from the primary knock-on region and forms IL even in the regions outside of the damage peak. This indicates that the effects of damage do not remain localized only in the primary knock-on region but spread even in the deeper area.

Fig. 7 shows the distribution of hydrogen and its com-

plexes, C_H, C_{VH} and C_{SH}. Due to a very high migration rate M_H hydrogen atoms also diffuse fast in the specimen. Hydrogen atoms reaching the surfaces escape from the specimens, while those meeting the sink such as vacancies in the knock-on region or impurity atoms are trapped by them and retained in the specimen.

4. Discussion

In the present calculations several rather important defect processes are neglected in order to simplify the model. We will discuss here the impacts of these assumptions on the calculated results described above and the limitation of the present calculations.

(1) The formation of larger complexes of vacancies and hydrogen atoms, mVnH (m, $n \geq 1$), is neglected. As one can see in Fig. 5, C_{VH} reaches about 10^{-2} in 100 s, because of the restriction of larger complex formation and a rather high binding energy. If the binding energy E^B_{VH} is low but some larger complexes such as V2H and V3H are thermally stable, most of the hydrogen atoms are trapped in these complexes. The large V–H complexes may act as a 'free vacancy killer' just as VH in the present calculations and therefore C_V remains at a constant level. The binding energy E^B_{VH} defined in the present calculation should be understood as an effective binding energy of vacancy–hydrogen complexes.

(2) Spontaneous clustering of neighboring vacancies neglected in the present model becomes important when C_V or C_{VH} reach the level of 10^{-2} even if the thermal mobility of V and VH is very low. In the good fitting case (Fig. 5), C_{VH} at the damage peak reaches this level in 100 s. The present model, therefore, cannot be applied to damage beyond several 100 s (0.1 dpa).

(3) I–H interaction is neglected. If we assume a strong binding energy between I and H, we can get dense IL meeting the experimental data, but it is impossible to obtain the prolonged C_I constant condition which is required to explain the linear growth of IL.

(4) The direct absorption of I by IL is also neglected. If the displacement collision sequence (DCS) encounters the dislocation core, the interstitial loop grows by absorbing the interstitial. The growth rate of this process is given by $2Pl_d$, where l_d is the length of DCS. If this is the major mechanism of loop growth, IL grows linearly under constant irradiation. The growth rate of this mechanism is, however, about 2×10^{-3} nm/s, which is about 1/20 of the observed growth rate. We can safely neglect the direct process.

5. Conclusions

According to the fusion relevant low energy hydrogen ion irradiation experiments, dense interstitial type dislocation loops are formed in many metals from the very low irradiation dose. In the case of Mo kept at room temperature the loops grow linearly under irradiation with a constant damage rate. In order to understand the characteristic defect, clustering processes under low energy hydrogen ion irradiation and the underlining defect interactions controlling the processes, accumulation of defects and defect–hydrogen complexes are calculated numerically using the homogeneous reaction kinetics and rate equations. These calculations do not consider the nucleation and growth of hydrogen bubbles which occur at high dose. The present calculations yield a very high concentration (order of 10^{-2}) of vacancy–hydrogen (VH) complexes and a high growth rate and relatively low concentration of interstitial loops (IL). These results are in disagreement with the experimental results. Within the framework of the present calculations, the experimental results could be explained, however, by postulating very low reaction efficiencies of interstitials with VH complexes and interstitial loops. This indicates that hydrogen atoms trapped in vacancies and dislocations prevent the reaction with free interstitials. Due to the low VH–I reaction, majority of the produced vacancies is accumulated as V–H complexes and thus lead to the formation of hydrogen bubbles at high dose, where the present rate equations cannot be applied.

The calculation also shows that the highly mobile interstitials and hydrogen atoms diffuse out from the primary damaged region and accumulated in the deeper region. It is expected that these defects degrade bulk properties of the materials.

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