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Cellular automaton model for hydrogen transport dynamics through metallic surface

K. Shimura [a,*], K. Yamaguchi [b], T. Terai [a], M. Yamawaki [a]

[a] *Department of Quantum Engineering and Systems Science, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

[b] *Japan Atomic Energy Research Institute, Shirakata 2-4, Tokai-mura, Naka-gun, Ibaraki-ken 319-1195, Japan*

Abstract

Hydrogen re-emission and re-combination at the surface of first wall materials are a crucial issue for the understanding of the fuel recycling and for the tritium inventory in plasma facing materials. It is know to be difficult to model the transient behaviour of those processes due to their complex time-transient nature. However, cellular automata (CA) are powerful tools to model such complex systems because of their nature of discreteness in both dependent and independent variables. Then the system can be represented by the fully local interactions between cells. For that reason, complex physical and chemical systems can be described by fairly simple manner. In this study, the kinetics of desorption of adsorbed hydrogen from an ideal metallic surface is modelled in CA. Thermal desorption is simulated with this model and the comparison with the theory of rate processes is performed to identify the validity of this model. The overall results show that this model is reasonable to express the desorption kinetics.

1. Introduction

Hydrogen re-emission and re-combination at the surface of first wall materials are a crucial issue for the understanding of the fuel recycling and for the tritium inventory in the plasma facing materials. Among a large number of studies, yet it seems to be difficult to model the transient behaviour of those processes due to its complex time-transient nature, which is comprised of mutual effects of different rate processes. Those processes include the diffusion inside the bulk, mass transfer between the bulk and the surface, surface migration, mass transfer between the surface and the gas. If one has to consider the effect of the surface conditions such as surface roughness, defects, and the existence of the surface contaminations, then the model becomes even more complicated. Even for the ideal cases, the surface appears to be an interface between the gas and the bulk in hydrogen–metal interactions. This means that, from the point of view from the hydrogen transport, the surface can be considered not only as a singularity but also a physical system. That is, the discontinuity of hydrogen potential through the surface, saturation of surface coverage and those distinct phenomenon occurs at the surface should also be considered for the generally applicable model. These are the reason that makes difficult for analytical modelling. Here arises a question that is how to include all of those effects into the model. Although the model of hydrogen–metal interactions is widely studied [1–4], those are rather unintuitive for such an application since those models handle the surface as only a simple boundary of the bulk diffusion so the applicability is restricted by the nature of the continuity of solution of differential equations. For the purpose of describing such systems, cellular automata (CA) are one of the very powerful tools [6–8] that have less restriction on conditioning the model compared

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[*] Corresponding author. Tel./fax: +81-3 5841 7420.

E-mail address: shimura@tokai.t.u-tokyo.ac.jp (K. Shimura).

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with some methods based on differential equation such as molecular dynamics. In general, CA are known as a discrete mechanical system which is fully discrete in both dependent and independent variables. The system can be represented by some sets of rules that describe the microscopic interactions based on the local concept. Moreover in CA, the control space is discretised into cells and the states of each of those cells are updated according to the states and the corresponding rules in each time interval. Because of such a microscopic viewpoint in contrast to the differential equation system, complex systems can be described by fairly simple manner. CA are also possible to imply highly non-linear boundary conditions in contrast to the model based on the differential equation. However there is not yet general way of finding the model for a system of interest. Hence creating the fundamental models in CA that follow the known elementary processes is the essential matter for further application and development. For the purpose of laying the groundwork for developing the generally applicable model of hydrogen transport in CA, the model of desorption of adsorbed hydrogen from the metallic surface is introduced since it is the one of the most important elementary surface processes. Then the calculations are performed to simulate a thermal desorption by using the model. Furthermore the verification of the model is carried on by comparison with the conventional method.

2. Modelling

The mechanism of desorption of hydrogen molecules from the metallic surface can be thought as consisting of three rate processes that are, (1) surface migration of adsorbed hydrogen atom, (2) encountering of two hydrogen atoms, (3) reaction to produce hydrogen molecule for desorption. All of those play important roles especially the surface migration due to its influence to the kinetics of desorption. However, the types of adsorption have to be distinguished when dealing with the surface migration. There are two types of adsorption that are physisorption and chemisorption. For physisorption, the H_2 molecules are held at the van der Waals potential minimum where several angstroms away from the surface. The physisorption energy is known to be fairly small and thus the mobility is very high but the residence time for physisorption is very short at higher temperature. Contrary to this, for chemisorption, the H_2 molecules dissociated to H atoms and make chemical bond between the hydrogen atoms and the metallic atoms at the surface and thus the energy for chemisorption is much higher than that for physisorption. Whereby the H atoms are located in the considerably deep potential well. It is considered that the potential well is evenly distributed on the ideal two-dimensional surface but there exists a sinusoidal potential variation throughout the surface. The adsorbed atoms hop around this variation via thermally activated process. The activation energy of surface migration is known as $\simeq 1/10$ of heat of adsorption [5]. During the surface migration, the possibility of desorption appears only when two atoms meet each other. Again a considering thermally activated process, the possibility of desorption is determined by the energy barrier for desorption. However, the desorption is expressed as:

$$H_{(\mathrm{ad})} + H_{(\mathrm{ad})} \rightarrow H_{2_{(\mathrm{g})}} + 2^{*}, \tag{1}$$

where subscript (ad) represents adsorbed, (g) represents gas phase and 2^{*} represents two empty sites on the surface.

While modelling the above desorption mechanisms, several assumptions have been made. There is always a sufficiently high pumping speed around the surface compared with the desorption rate, so that the increase in pressure at any instant is proportional to the desorption rate. No precursor state is considered. The surface migration is considered to be a random walk. The hydrogen transfer between the bulk and the surface is also not considered since the purpose of this work is to create the Ca model of such a system that accurately follows the conventional expression. Although the effect of the bulk diffusion can easily be implemented, as to the verification of the model, step by step verification of such an elementary process is fundamentally important prior to summing several elementary processes especially when modelling in CA that the verification method is limited.

However the CA model is constructed as follows. At first, the two-dimensional surface is divided into a square lattice like a chessboard. Each lattice has got two stats that are black or white. When it is black it means that there exists an adsorbed hydrogen and white means the site is empty. Transition rules are applied throughout the surface via a 2 × 2 block so called ‘Margolus block’ with two sets of rules, one for surface migration and another for desorption.

The surface migration is at first modelled as follows. As it is mentioned, this process is considered as random walk diffusion. The CA model for such system is widely studied [6,7]. Chopard and Droz [6] introduced a model in which diffusion is realised via rotation of the Margolus block. Their algorithm, such as rotating the Margolus block clockwise and anticlockwise with equal probability of 1/2 as shown in Fig. 1, satisfies the phenomenological diffusion equation. This algorithm is utilised to express the surface migration. Secondly, desorption is modelled as follows. When there are two occupied sites inside a Margolus block, those are entitled for desorption by reacting each other. The probability for this process is determined in accordance to thermally activated process that is, comparing the energy resulting

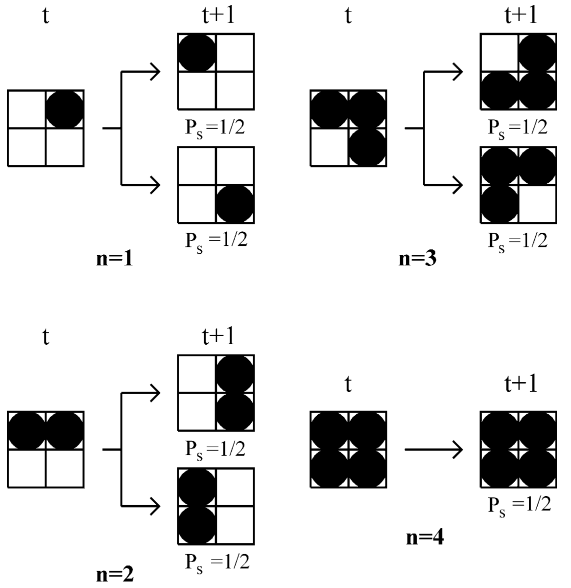

Fig. 1. Transition rules for surface diffusion [6], where n denotes the number of occupied sites in the Margolus block, P_s denotes the transition probability and t denotes time.

from the fluctuation of the thermal vibration E_s with the energy barrier for desorption E_{des}. Then the transition takes place when E_s is larger than E_{des}. Fig. 2 illustrates the transition rules for desorption for various conditions. These rules show that, inside the Margolus block, desorption can only occur with the given probability P_{des} when adjacent cells are occupied. Then P_{des} is given as follows:

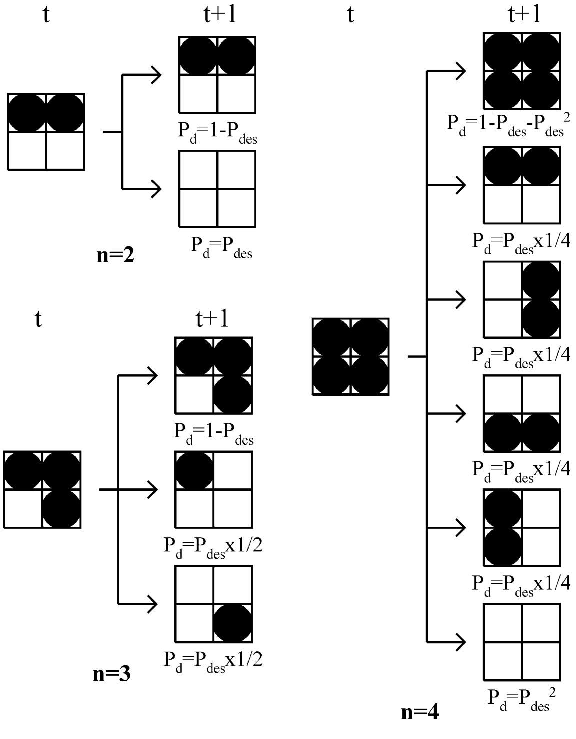

Fig. 2. The transition rules for desorption, where P_{des} denotes the probability of desorption.

$$P_{des} = \frac{\max(E_{des}, E_s) - E_{des}}{E_s - E_{des}}, \tag{2}$$

where, $E_s = -RT\ln(a/\tau v)$, a denotes the random number with uniform distribution between 0 and 1, τ denotes the time interval of each step and v denotes the frequency factor.

The calculation is to be carried out through the algorithm such that in each even time step, the surface is scanned through with the Margolus block and the above rules are applied. For odd time steps, the grid defining the blocks is shifted along a diagonal by 1/2 block and rules are applied. The next step is to put the shifted grid back to the original position and start even time step. This iteration is done until given conditions are satisfied.

3. Results and discussion

The verification of the model can be performed by comparison between the results obtained under the same conditions of this model in CA and the known conventional approach based on differential equation. The above model is calculated to simulate thermal desorption with constant temperature elevation rate. Simulating thermal desorption is considered to be a suitable way to verify the model since it is the transient expression in both time and temperature. At first, following initial conditions are considered. Initial coverage is 0.6, activation energy of desorption and the frequency factor are assumed as constant and they are 96.5 kJ/mol H_2 and 10^{12}/s, respectively. Then various temperature elevation rates are taken as 0.5, 1, 2 and 4 K/s. Additionally, the lattice of 1000×1000 sites with periodic boundary conditions and 0.125 s of time step is used. The results are shown in Fig. 3.

Due to the nature of stochastic CA, numbers of calculations have performed for each condition to obtain the average. In this simulation, a calculation is performed 10 times for each condition as it is seen from the figure. The results show that, at the earlier stage of temperature elevation, sufficient hydrogen atoms existing on the surface for reaction and thus desorption rate is highly characterised by the Boltzmann factor but it is considered as independent of temperature elevation rate. Then, the desorption rate increases rapidly as temperature rises and consequently, the surface coverage decreases with nearly the same rate. This means that the possibilities of encountering two atoms are also reduced

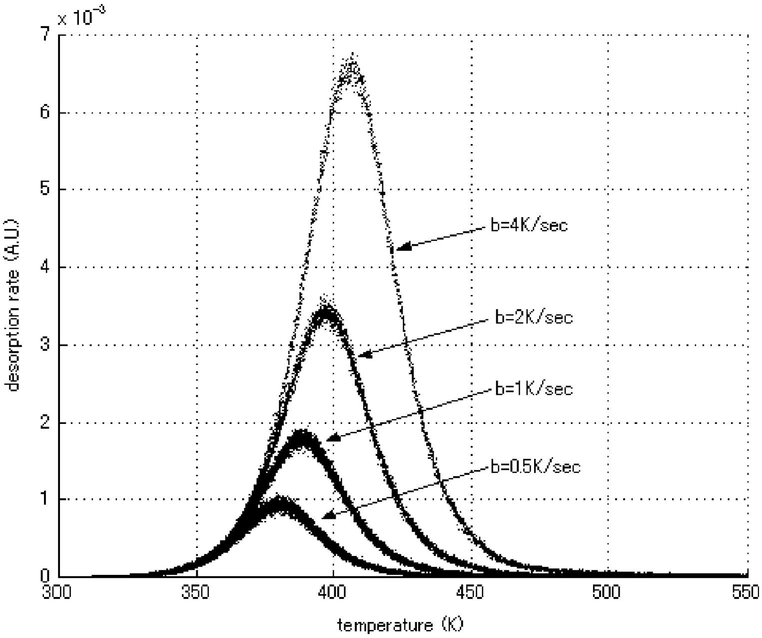

Fig. 3. Results of CA simulation for the conditions; initial coverage $\theta_0 = 0.6$, activation energy of desorption $E_{\mathrm{des}} = 96.5$ kJ/mol H_2, frequency factor $v = 10^{12}$/s, temperature elevation rates $b = 0.5$, 1, 2 and 4 K/s.

simultaneously. This reduction causes to reduce the rate of increase of desorption rate and finally the maximum peak appears. Up to this point, desorption rate is dominated by the Boltzmann factor which represents the probability of reaction of two hydrogen atoms to produce a molecule. From this point of view, the peak can be considered as a turning point of whether the rate is determined by hydrogen reaction or surface coverage. In general it is known that the surface coverage at the peak is nearly the half of its initial value, and this nature causes the shift in peak temperatures for various temperature elevation rate. However, after a peak appears, desorption rate starts decreasing rapidly along with an increase in temperature. At this stage, it can be thought that the rate of encountering two H atoms as the rate-determining step which is dominated by the surface coverage at the instant. Finally, most of the adsorbed atoms are desorbed and desorption rate is back to nearly zero. It is also observed that the integration value of each curve is nearly equal to the value of its initial coverage.

The above characteristics can also be seen from the approach via the theory of rate processes. The well known expression for thermal desorption spectrum is the Polanyi–Wigner equation which is as follows:

$$-\frac{\mathrm{d}\theta}{\mathrm{d}t} = v \exp\left(-\frac{E_{\mathrm{des}}}{RT}\right)\theta^n, \tag{3}$$

where, θ denotes the coverage, t denotes time, v denotes frequency factor, E_{des} denotes the activation energy of desorption, R denotes the gas constant, n denotes the order of desorption reaction and T denotes temperature.

The order of desorption reaction is usually assumed as 2nd order for hydrogen atoms on the metallic surface. When the temperature is linearly elevated, T is given as $T = T_0 + bt$, where b is the temperature elevation rate and t represents time. Eq. (3) is calculated for the same condition as those for CA and is illustrated in Fig. 4. It is seen from Figs. 3 and 4, very close qualitative agreement can be observed. This agreement shows that this CA model is consistent with the conventional approach, the theory of rate processes. Consequently this algorithm is reasonable to express the kinetics of the thermal desorption spectrum. One question arises here is the time dependence of the result. Often, this kind of simulation is difficult to realise the results in proper time domain. In many cases, the simulation results are shown in terms of calculation steps. Here in this result, the desorption rates are expressed in terms of temperature which is a function of time. The validity of the result in terms of time can be confirmed by focusing on the peak temperature. The peak temperature obtained from this CA model and the Polanyi–Wigner model is compared in Table 1. It is obvious that the peak temperatures are in good agreement. The small fluctuations in those values are due to the variation of random processes in

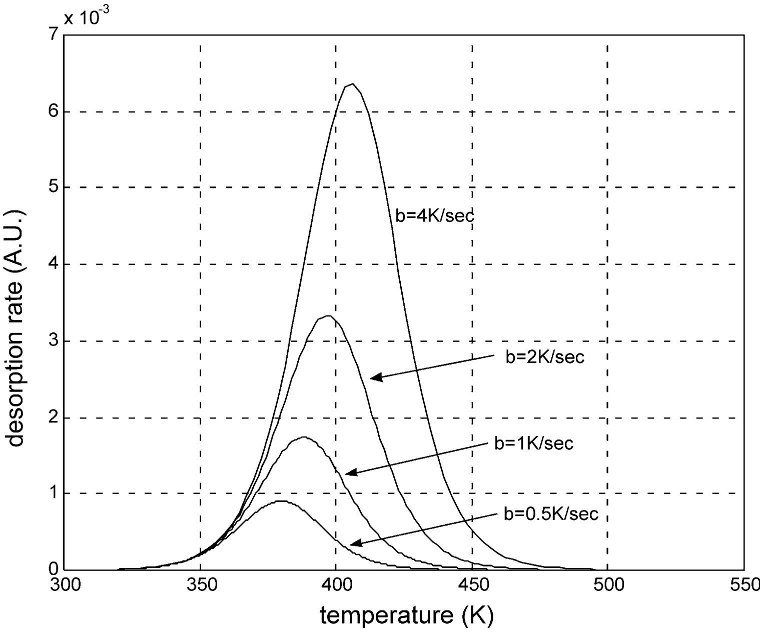

Fig. 4. The results of numerical calculation of the Polanyi–Wigner equation. The parameters used for this calculation are the same as those for Fig. 3.

Table 1
Peak temperature for Polanyi–Wigner (P–W) and CA results under various temperature elevation rates (TER)

	TER (K/s)			
	0.5	1	2	4
P–W (K)	380	388	397	407
CA (K)	381	390	399	409

the algorithm. While the numerical calculation of the differential equation is widely accepted as its result can be expressed in proper time domain, the result obtained from this model is in good agreement with it. This fact also backs up the reasonability of this CA simulation in proper time domain. Furthermore, the Arrhenius plot is made from the results of the CA simulation in order to determine the activation energy of desorption. Eq. (3) can be rearranged to express the peak such that $\mathrm{d}^2\theta/\mathrm{d}t^2 = 0$:

$$2\ln(T_p) - \ln(\beta) = \frac{E_{\mathrm{des}}}{RT_p} + \ln\left(\frac{E_{\mathrm{des}}}{Rvn\theta_p^{n-1}}\right), \tag{4}$$

where subscript p denotes the value of corresponding variables at the peak.

This procedure is to identify the self-consistency of this model. Fig. 5 illustrates the Arrhenius plot while circles show the peaks of each calculation that are performed 10 times for each temperature elevation rate and the straight line illustrates the least square fitting of those peaks with respect to Eq. (4). The corresponding activation energy of desorption can be determined from the gradient of this line. The value obtained is 94 kJ/mol H_2. The activation energy of desorption which is given for this simulation is 96.5 kJ/mol H_2. This agreement shows the self-consistency of this model, although the value is not exactly coincident. This can be thought that the difference in the value is mainly caused by the variation of the random process and discreteness of the algorithm. One effective way of reducing such difference is to increase the number of cells and number of calculations for each condition. However, the determination of the exact asymptotic value is currently very difficult due to lack of a mathematical theory that can solve the global behaviour for the particular CA model. In another word, the general method of finding exact solutions for arbitrary defined CA has not been established yet although CA are widely accepted in many fields. Thus the verification of the model must be carefully carried out with physical, mathematical and experimental considerations.

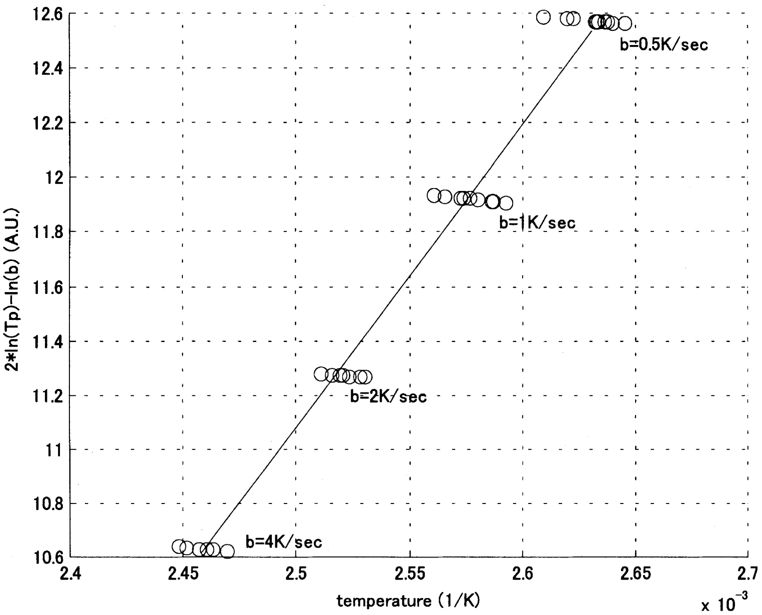

Fig. 5. The Arrhenius plot obtained from the results of CA.

4. Conclusions

The kinetics of desorption of adsorbed hydrogen from an ideal metallic surface is modelled in CA. The thermal desorption spectrum is simulated with this model for various temperature elevation rates. Then the results are compared with those obtained from the theory of rate processes. The qualitative agreement observed in the simulated desorption rate. The quantitative agreement has also seen in the peak temperature. Thus the simulation is found to be valid for the expression in proper time domain. Also the activation energy of desorption is calculated from the simulated spectrum via an Arrhenius plot, then the value given for the simulations and the value obtained from the results are found to be in a good agreement. Therefore the self-consistency of this model is confirmed. The overall results show that this model is reasonable to express the desorption kinetics by CA. However, when modelling the hydrogen transport, the surface is usually treated as the boundary of bulk diffusion. In this way, the expression of the surface is quite different from the two-dimensional plane. Hence it is difficult to implement all of the surface processes into the model with bulk diffusion. This work shows that the possibility of such difficulty can be resolved by use of CA that has rather microscopic point of view since the surface can be handled as proper two-dimensional plane. Finally, the practical application of the CA model to fusion can be foreseen, although this model only represents one of the desorption kinetics in the present study since this model can be easily combined with models of other surface processes as well as bulk diffusion.

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