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The Tribosorption of Hydrogen to Silicon Carbide

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The tribosorption of hydrogen into granular silicon carbide was studied under shaking in the pressure range of 0.04—1 Torr at room temperature. The sorption was observed when the frequencies of the vibration were 10.0 and 13.3 Hz, but was not observed when they were 0 and 6.7 Hz. The rate of tribosorption evaluated from the change in the pressure of gas had its maximum value when the sample was shaken for 20—40 h. It was found that this tribosorption could be attributed to an absorption to the solid and could be treated as a diffusion process. The time dependence of the diffusion coefficient showed a behavior similar to that of the lattice defect. It is suggested that the chemical properties of hydrogen and the activation of the solid play important roles in the tribosorption process.

Chemical reactions generally take place by the absorption of heat, radiation, *etc.* On the other hand, reactions have been known to be similarly induced by mechanical treatments of a solid, *e.g.*, by friction, compression, or impact.[1,2)] That is to say, such mechanical workings gradually produce various disturbances in the crystal lattice, such as bond rupture, irregular atomic displacement, strain, and lattice defect, and chemical reactions or phase transitions proceed in and on the solid. In the last one and a half decades Heinicke and his co-workers[3–5)] have made an extensive study of tribochemical reactions, especially in the presence of gases, through phenomenological observations of the reaction and measurements of lattice disorders induced in the solid, and so on. In addition, the relations between the so-called tribosorption and the tribochemical reactions have been discussed by them.

In tribochemistry many parameters participate in a reaction, so that it is necessary to select the most simple reaction system in order to obtain reproducible experimental results and to clarify the reaction mechanism. In this sense, a homomolecular isotopic exchange reaction is considered to be one of the most probable. Therefore, a study of a hydrogen–deuterium gas system, $H_2+D_2=2HD$, was made under the mechanical treatment of granular silicon carbide,[6)] and an increase in the reaction rate with the shaking time was found. For a further discussion of the experimental results, and investigation of tribosorption is necessary.

Recently Heinicke *et al.*[7)] investigated the tribosorption of the system consisting of powdered silicon carbide and hydrogen. They dealt mainly with the primary and secondary changes in the structure produced in the silicon carbide powder during mechanical working in the presence of hydrogen; they found a close correlation between the disturbances in the lattice and the amount of tribosorption. However, an analysis of the sorption process itself has been scarcely done.

In the present paper, the tribosorption of hydrogen into granular silicon carbide was carried out with the intention of analysing the sorption process kinetically, and some discussion is given of the mechanism of the tribosorption.

Experimental

The silicon carbide (Showa Denko K. K.) employed was black, *ca.* 1.2 mm in granular size, 98.5% pure; it was α-SiC in the hexagonal crystal system. One to twenty grams of SiC, which had been evacuated at 850 °C for a period of more than 10 h, was shaken in a 100 ml quartz vessel by a Irie Model TS-3 shaker in 0.04—1 Torr H_2 at room temperature; its amplitude was 10 mm, and the vibrational frequencies were 6.7, 10.0, and 13.3 Hz. The sorption rate was measured through the continuous measurement of the pressure change of H_2 in the system (total volume: 1.3 l) by a Pirani gauge. The existence of the reaction products was checked by means of a Hitachi Model RM-50 mass spectrometer.

In order to observe the changes of the SiC granules with the shaking, their surface area was measured by the BET adsorption method using krypton at the boiling point of liquid nitrogen, and the changes in their surface state were photographed with the aid of a JEOL Model JSM-15 scanning electron microscope.

Results and Discussion

Tribosorption Rate. When the granular SiC was left at room temperature in H_2 without shaking, no sorption was observed. On the other hand, when the mechanical treatment was used, the pressure of H_2 decreased, and tribosorption was observed. This sorption rate showed a steep increase in the initial stage of the shaking time; it reached its maximum value near 20 to 40 h, after which there was a monotonous decrease (Fig. 1). In a usual sorption which takes place ther-

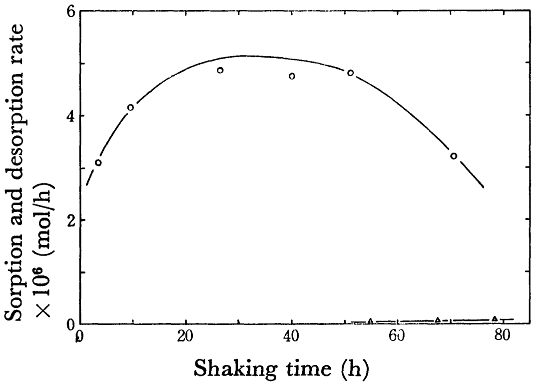

Fig. 1. The shaking time dependence of the sorption rate at 0.04—1 Torr and the desorption rate: Vibrational frequency $f=13.3$ Hz; weight of SiC $W=10$ g. ○, sorption rate; △, desorption rate.

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mally, no such maximum of the sorption rate is observed generally. Consequently, the appearance of this maximum may be considered to be one of the most important features of the tribosorption.

Prior to the investigation of the tribosorption mechanism, the contributions of the inner wall of the quartz vessel and the quartz powder which might be produced by abrasion to the observed tribosorption were examined. First, in order to see the effect of the inner wall of the vessel, the effect of the amount of SiC on the sorption rate was investigated. The sorption rate was found to be proportional to the amount of SiC (Fig. 2).

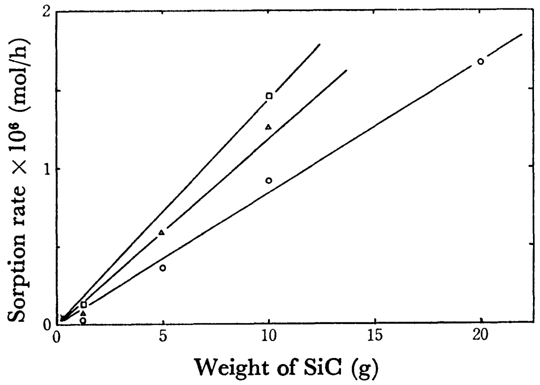

Fig. 2. The effect of SiC amount on the sorption rate: f=10 Hz; hydrogen pressure P=0.04—1 Torr. Shaking time: ○, 3 h; △, 10 h; □, 30 h.

Then, tribosorption was carried out by adding the quartz glass powder to SiC. The sorption in this case showed no increase but, rather, a little decrease compared with that in the case free from additives (Fig. 3). From the results of these experiments, it can be seen that the sorption occurred exclusively on SiC.

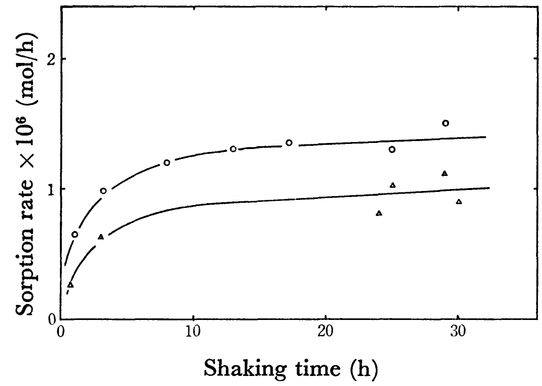

Fig. 3. The effect of quartz glass powder on the sorption rate: f=10 Hz; P=0.04—1 Torr. ○, SiC 10 g; △, SiC 10 g+glass powder 10 mg.

Next, it is necessary to distinguish whether the sorption is due to adsorption or absorption. For this purpose, the sorption rate was measured in two regions of H_2 pressure, namely, 0.02—0.2 and 5—15 Torr. In spite of the pressure difference of a factor of about 100, the ratio of the two sorption rates was merely about 2:1. This result indicates that the pressure dependence of the sorption rate is effectively nil; hence, the surface of SiC is always saturated with hydrogen. Heinicke *et al.*[4] also showed that the adsorption was very fast and immediately attained equilibrium when CO_2 was tribosorbed into metals. If the observed sorption was due chiefly to adsorption, the shaking time dependence of the sorption amount should, therefore, correspond to that of the surface area of SiC. The measurement of the surface area resulted in an initial rapid increase and a subsequent slower one, while the sorption amount had an induction time at the same initial stage (Fig. 4). Consequently, there is no simple correspondence between the two.

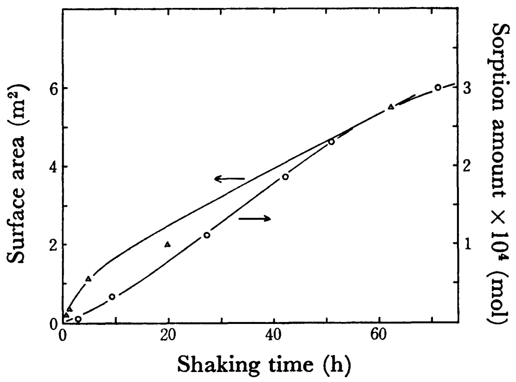

Fig. 4. The variations of the sorption amount and the surface area of SiC with shaking time: f=13.3 Hz; P=0.04—1 Torr; W=10 g. ○, sorption amount; △, surface area of SiC.

If this sorption is mainly absorption, the rate of resorption on SiC which, after the sorption experiment for a long period, has been evacuated under shaking to make the concentration near the surface vanishingly small, can be expected to be at its maximum at the beginning, to decrease slowly, and finally to attain the value extrapolated from the first run. Our measurement of the re-sorption after the 160 h tribosorption gave the result just anticipated, and the sorption rate attained the extrapolated value after 20 h (Fig. 5). In addition, Henning[8] showed that SiC absorbed about 10 times of the monolayerly adsorbed amount of H_2; Heinicke *et al.*[4] also reported that absorption occurred in many tribochemical processes. On the basis of these

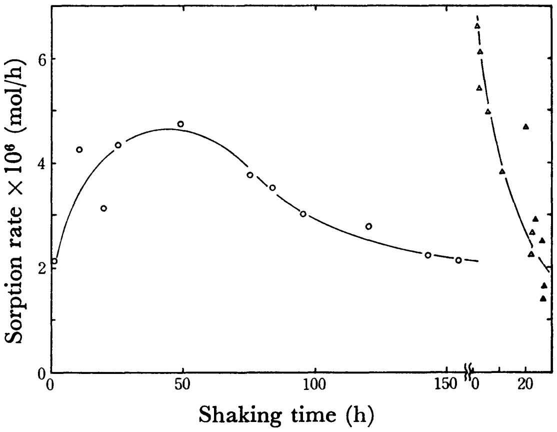

Fig. 5. The resorption rate of triboevacuated SiC after long time sorption: f=10 Hz; P=5—15 Torr; W=20 g. ○, sorption rate; △, resorption rate.

facts, it can be seen that the observed tribosorption results mainly from the absorption phenomenon.

Analysis of the Tribosorption Curves. Considering that the adsorption rate on the SiC surface was very rapid and that the re-sorption rate attained the extrapolated original value after a considerably long time, about 20 h, as is shown in Fig. 5, the tribosorption attributed to an absorption may be treated as a diffusion process. However, the diffusion coefficient obtained from the sorption rate may include the effects of the quartz glass powder and the tribo-desorption. As has previously been mentioned, the quartz glass powder caused a slight decrease in the sorption rate (Fig. 3). However, the amount of powder produced, which was estimated from the weight change in the vessel in each sorption experiment, was considerably less than the quantity added in the run shown in Fig. 3. Therefore, the effect of the quartz powder can be virtually neglected. If it is clearly seen that the already absorbed hydrogen and the tribochemical reaction products are desorbed from the SiC surface during the tribosorption, the sorption rate evaluated from the pressure change in the gas phase does not give a true value. However, SiC which had just been subjected to a tribosorption experiment exhibited a very small tribo-desorption rate (Fig. 1), and the results of a mass-spectrometric analysis of the gas which remained in the vessel after the sorption experiment under conditions favorable for the formation of the reaction products indicated the presence of only small amounts of methane and ethane, with a large amount of hydrogen. In addition, all the gas in the system was evacuated and H_2 was refreshed within 15 h in the sorption experiments. Therefore, the tribo-desorption may be thought to influence the sorption rate scarcely at all.

Absorption rate decreases monotonously in a usual simple diffusion system. However, a maximum in the rate can be expected in the case of a varying surface concentration or in the case of a varying diffusion coefficient with the time.[9] The former is inapplicable to the present case because of the rapid adsorption rate and because of the quick attainment to the saturated surface concentration. The following discussion will be concerned with the latter case.

In the tribosorption, the structures and properties of the solid will change during the shaking. Thus, the diffusion coefficient changes with the time. A more quantitative analysis is performed through the application of Fick's diffusion equation to the observed sorption rate by regarding the SiC granule as a sphere. Two assumptions are adopted here; one is that the radius of the granule does not vary during the shaking, and the other is that H_2 is absorbed mainly by the granular SiC and not by the powdery SiC produced during the shaking. Actually, neither the variation in the granular size nor the presence of large broken pieces was much observed after the tribosorption. Furthermore, granular SiC (10 g) was shaken with powdery SiC (0.44 g), but the sorption rate was scarcely influenced at all. Consequently, the above two assumptions seem reasonable. Then, in case of radial diffusion in a sphere of radius a, the equation takes this form:[10]

$$\frac{\partial U}{\partial t} = D\frac{\partial^2 U}{\partial r^2}, \tag{1}$$

where t is the diffusion time; D, the diffusion coefficient; r, the distance from the center of the sphere, and $U=Cr$, where C is the surface concentration. When the diffusion coefficient depends on t, T is defined as follows:

$$\mathrm{d}T = D\mathrm{d}t. \tag{2}$$

Under the following conditions:

$$\begin{array}{lll} U=0 & r=0 & t>0, \\ U=aC & r=a & t>0, \\ U=0 & 0<r<a & t=0, \end{array} \tag{3}$$

the solution of Eq. (1) is given by:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-n^2\pi^2 T/a^2\right), \tag{4}$$

where M_t and M_∞ are the sorption amounts at the times of t and infinity respectively.

Here let us deal with the case shown in Fig. 1. It is assumed that each unit cell of SiC can finally absorb one hydrogen atom ($M_\infty=30$ mmol as H_2) and that, from the granular size, a^2 is equal to $3.6\times10^{-7}\ \mathrm{m}^2$. When M_t observed at t is substituted into Eq. (4), the time dependence of the diffusion coefficient is obtained by Eqs. (2) and (4) (Fig. 6). In the above treatment, if the surface area effective for diffusion increases with the time, the apparent value of D should vary. The surface area observed by the BET method increased by a factor of about 10 during 60 h (Fig. 4). On the other hand, as has previously been described, the sorption rate in the case of adding powdery SiC was approximately equal to that without the powder. Accordingly, we may consider that the enlargement of the surface area observed is mainly attributable to the production of powdery SiC and powdery quartz glass, and that this increase scarcely contributes to the enlargement of the surface area effective for diffusion. It can, therefore, be understood that the time dependence of D results exclusively from that of the activity of the solid for diffusion. In fact, a scanning electron microscope showed that, at least on the surface, roughness grew during the tribosorption (Fig. 7).

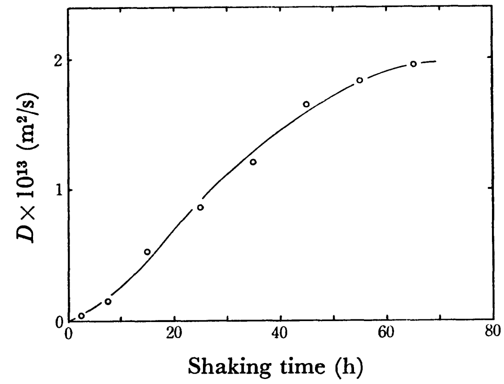

Fig. 6. The shaking time dependence of the diffusion coefficient calculated from Eqs. (2) and (4).

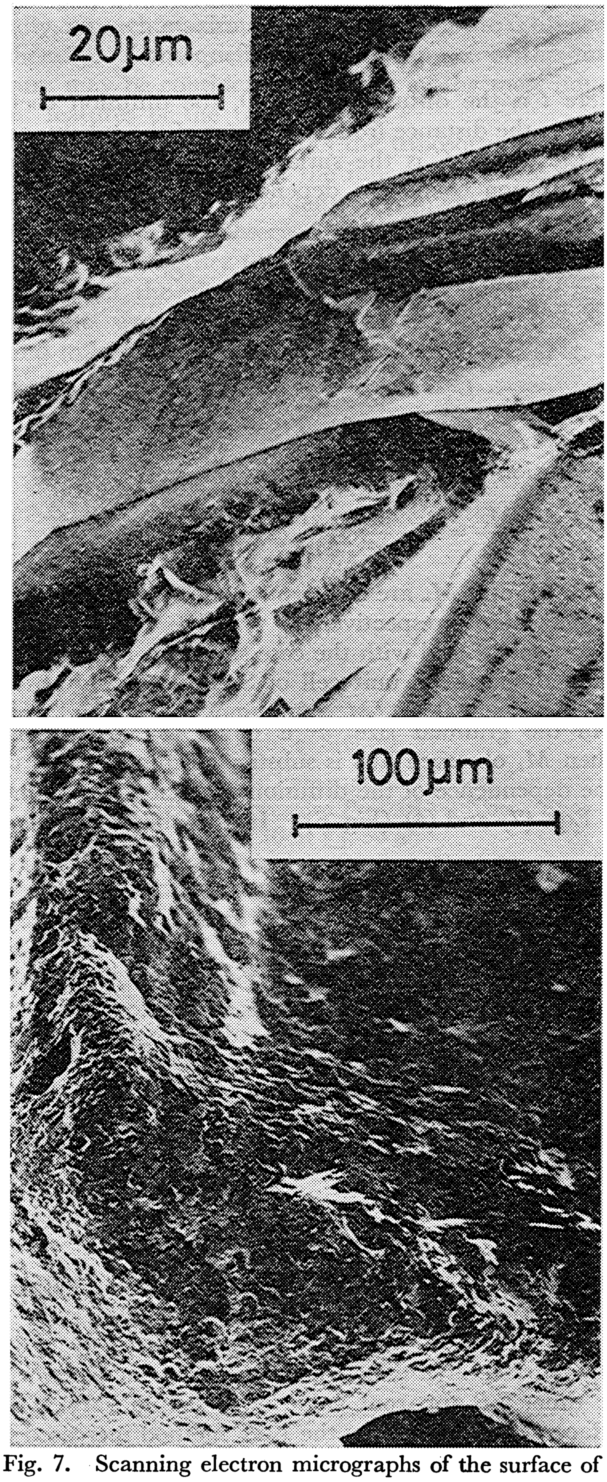

Fig. 7. Scanning electron micrographs of the surface of SiC: (a), before shaking; (b), after shaking.

Heinicke *et al.*[7] carried out the experiments of X-ray diffraction and ESR, together with the tribosorption of H_2 on SiC powders, and measured quantitatively the changes in the disturbances of the solid, such as the size of the primary grain, the disorder of the lattice, and the concentration of the free radical, *etc.* of SiC. In thier experiments all these disturbances exhibited similar time dependence, and their patterns were analogous to that of D obtained in our experiment. In particular, the disorder of the lattice is regarded as an activity which indicates the ease of hydrogen diffusion in the solid. From this point of view, too, it may be reasonable that the diffusion coefficient exhibited the variation shown in Fig. 6.

The powder system used by Heinicke *et al.*[7] had no maximum in its tribosorption rate, but only a monotonous decrease. In this regard, our experimental results differ from theirs. This probably comes from the difference in experimental condition; the granular system in the shaker and the powder system in the ball mill. In terms of the amounts of hydrogen absorbed at the same shaking time, the value obtained by Heinicke *et al.* was greater than ours by a factor of about 100. There may also be a maximum in the sorption rate at the very initial stage in their powder system.

Mechanism of the Diffusion. Then the sorption experiments of inert gases were carried out in a similar manner to ascertain whether the sorption process of SiC–H_2 system is a physical or chemical one. Helium, with a smaller molecular radius than hydrogen, and krypton, with a larger, were used, and neither of them was tribosorbed at all. Therefore, it may be seen that the sorption process of hydrogen proceeds not as a merely physical one but as a process with chemical interaction between SiC and hydrogen. Further, when deuterium was subjected to the sorption experiment, the isotope effect was not found. This information suggests that the activation step of diffusion needs an extremely high energy. Thus, as the mechanism of the tribodiffusion of hydrogen in SiC, it may be assumed that H_2 is dissociated into atomic hydrogen at high-energy points, *e.g.*, the lattice distortion and the so-called magma plasma which are produced by the collision of solids, and that the atomic hydrogen diffuses into the distorted lattice with chemical bonding processes.

As has previously been mentioned, the sorption rate was independent of the H_2 pressure and proportional to the SiC weight (Fig. 2). The surface area effective for the diffusion and activity of SiC are usually functions of the time. Therefore, D may be expressed as follows:

$$D = kP^0WA(t)S(t), \tag{5}$$

where k is the constant; P, the gaseous pressure; W, the weight of SiC; A, the activity of the solid for diffusion, and S, the effective specific surface area. In addition, considering the vibrational frequency, no sorption was observed at 6.7 Hz, and the sorption rate at 10 Hz was one-third of the sorption rate at 13.3 Hz. The variation in the vibrational frequency seems to influence in a complicated manner the diffusion coefficient through A, S, and the activation of hydrogen.

There may be much problems in the application of Fick's equation to such a complex process as tribosorption. In the present case, all the factors due to rough approximation must be included in the activity, A, of Eq. (5). However, A and the distortion of the solid showed similar patterns in their time dependences. Hence, this treatment is correct, at least qualitatively.

In conclusion, the tribosorption of H_2 into SiC can be interpreted as a diffusion process which is essentially chemical in its nature. The diffusion coefficient in this case varies during the shaking; its variation may be caused by the activity change in the solid under mechanical treatment in the presence of H_2.

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