Using An Extended Tersoff Interatomic Potential to Analyze The Static-Fatigue Strength of SiO₂ under Atmospheric Influence*

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Calculations of SiO₂ static-fatigue strength are used to show that the strength-degradation behavior of the material under the influence of the ambient atmosphere can be analyzed using an interatomic potential which is based on the Tersoff potential but extended to take charge transfer effects into account. The force-elongation curves of the Si-O interatomic bonds of the SiO₂ are calculated with and without H₂O in the atmosphere. Based on these curves, crack propagation behavior is analyzed, and calculated results are shown to correspond well with experimental results. Moreover, the calculated values of the strength decrease caused by the H₂O also show fair agreement with the experimental values.

Key Words: Computational Mechanics, Molecular Dynamics, Crack Propagation, Interatomic Potential, Atmospheric Influence, Static Fatigue, Silicon Oxide

1. Introduction

Degradation of various different materials and the interfaces between them is one of the most challenging problems in the design of various semiconductor devices⁽¹⁾. This is because the degradation behavior is complicated by the simultaneous action of stress and interaction with the atmosphere, and is therefore difficult to predict. Atomic-level simulations promise to become effective tools for clarifying the mechanisms of such degradation, because the degradation is essentially caused by atomic level processes.

Some degradation processes have already been made clear by atomic level simulations⁽²⁾. For example, the initiation and growth of grain-boundary defects caused by stress have been investigated and some interesting results have been obtained⁽³⁾. Despite their importance, however, simulation methods taking into account the influence of atmosphere have not yet

been established.

There are two ways in which atomic level simulation methods may advance hereafter⁽⁴⁾. One is the use of strict ab-initio methods. The other is the use of practical empirical methods. We can expect that the latter will produce the most powerful tools for engineering use in the near future, because it already enables us to calculate problems of practical size easily. The former, strict methods, require enormous computational power. In this paper, therefore, an empirical method is investigated: one which enables to analyze the behavior of the degradation under the simultaneous influence of stress and atmosphere.

To take atmospheric influences into account, an interatomic potential energy function (hereafter called "interatomic potential") is needed which can express the interaction between the atoms comprising a solid and the surrounding atmosphere. Conventional classical interatomic potentials, however, can not express this interaction⁽⁵⁾. In this paper, therefore, I propose to use an interatomic potential⁽⁷⁾ created by extending the interatomic potential proposed by Tersoff⁽⁶⁾ to include the effects of charge transfer between atoms.

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As a target problem, I will investigate static fatigue of SiO₂ in an H₂O atmosphere. Silicon oxide, SiO₂, is one of the essential materials that make up semiconductor devices, and its degradation is one of the most important issues related to maintain integrated circuit reliability.

The static fatigue strength is known to be drastically decreased by the presence of water, and a model for explaining this behavior has been proposed by Michalske and Freiman⁽⁸⁾. Their model says that H₂O molecules, which penetrate the crack like faults in the SiO₂ and reach their tips, accelerate the breaking of the Si-O atom bonds there by reacting with them. Their model is, however, qualitative and not quantitative. In this paper, I will perform a quantitative investigation by extending their model.

The paper is organized as follows. At first, in section 2, the extended Tersoff interatomic potential is presented which enables us to take the atmospheric influences into account. Next, in section 3, breaking behavior of crack-tip atomic bonds is investigated using this potential. Then, in section 4, macroscopic crack extension behavior is calculated based on this bond-breaking behavior, and the results are compared with experimental observations. In section 5, I discuss the obtained results, and finally, in section 6, I summarize the conclusions we have reached.

2. The Interatomic Potential

One of the most serious faults of conventional interatomic potentials is their neglect to take into account the effects of changes in coordination numbers and of interatomic charge transfers caused in the process of reaction between atoms of different species, such as atoms in solids and in their atmosphere. Recently, Tersoff⁽⁶⁾ developed an interatomic potential which takes the effects of coordination number changes into account. Adding terms which express the effects of the charge transfer to his potential, I previously proposed an interatomic potential (extended Tersoff potential)⁽⁷⁾.

The potential function and its verification are explained in sections 2.1 and 2.2, respectively.

2.1 The potential function

The proposed potential function is expressed as follows:

$$U_T = \sum_i \sum_j u_{ij}/2 + \sum_i \phi_i, \quad (1)$$

$$\phi_i = [(I_{Ei} + A_{Ei})/(2c)]q_i + [(I_{Ei} - A_{Ei})/(2c^2)]q_i^2, \quad (2)$$

$$u_{ij} = u_{REPij} + u_{SHTij} + u_{IONij} + u_{VDWij}, \quad (3)$$

$$u_{REPij} = f_{Sij} A_{ij} \exp(-\lambda_{ij} r_{ij}), \quad (4)$$

$$u_{SHTij} = -f_{Sij} b_{ij} B_{ij} \exp(-\mu_{ij} r_{ij}), \quad (5)$$

$$u_{IONij} = f_{Lij} \eta_i \eta_j q_i q_j / (4\pi \epsilon_0 r_{ij}), \quad (6)$$

$$u_{VDWij} = -f_{Lij} \sqrt{(C_{VDWi} C_{VDWj})} / r_{ij}^6, \quad (7)$$

$$b_{ij} = [1 + (\beta_i \sum_k \xi_{ijk})^{n_i}]^{-1/(2n_i)}, \quad (8)$$

$$\xi_{ijk} = f_{Sik} \exp[\mu_{ij}^m (r_{ij} - r_{ik})^m] \times \{1 + c_i^2/d_i^2 - c_i^2/[d_i^2 + (h_i - \cos \theta_{ijk})^2]\}, \quad (9)$$

$$f_{Sij} = f_c(r_{ij}, \sqrt{(R_{Si} R_{Sj})}, \sqrt{(S_{Si} S_{Sj})}), \quad (10)$$

$$f_{Lij} = f_c(r_{ij}, \sqrt{(R_{Li} R_{Lj})}, \sqrt{(S_{Li} S_{Lj})}), \quad (11)$$

$$f_c(r, R, S) = 1, \quad (\text{in the case of } r \leq R) \quad (12.a)$$

$$f_c(r, R, S) = 1/2 + (1/2) \cos[\pi(r - R)/(S - R)], \quad (\text{in the case of } R < r < S) \quad (12.b)$$

$$f_c(r, R, S) = 0, \quad (\text{in the case of } r \geq S) \quad (12.c)$$

$$\lambda_{ij} = (\lambda_i + \lambda_j)/2, \quad (13)$$

$$\mu_{ij} = (\mu_i + \mu_j)/2, \quad (14)$$

$$A_{ij} = \sqrt{(A_{Si} A_{Sj})}, \quad (15)$$

$$B_{ij} = \sqrt{(B_{Si} B_{Sj})}, \quad (16)$$

$$A_{Si} = A_i \exp(\lambda_i D_i), \quad (17)$$

$$B_{Si} = B_i \exp(\mu_i D_i) \cdot [a_{Bi} - |b_{Bi}(q_i - Q_{oi})|^{n_{Bi}}], \quad (18)$$

$$D_i = D_{vi} + |b_{Di}(Q_{vi} - q_i)|^{n_{Di}}, \quad (19)$$

$$b_{Di} = (D_{Li} - D_{vi})^{1/n_{Di}} / (Q_{vi} - Q_{Li}), \quad (20)$$

$$n_{Di} = \ln[-D_{vi}/(D_{Li} - D_{vi})] / \ln[Q_{vi}/(Q_{vi} - Q_{Li})], \quad (21)$$

$$b_{Bi} = |a_{Bi}|^{1/n_{Bi}} / \Delta Q_i, \quad (22)$$

$$a_{Bi} = 1/(1 - |Q_{oi}/\Delta Q_i|^{n_{Bi}}), \quad (23)$$

$$Q_{oi} = (Q_{vi} + Q_{Li})/2, \quad (24)$$

$$\Delta Q_i = (Q_{vi} - Q_{Li})/2, \quad (25)$$

where U_T is the total potential energy of the system consisting of all atoms in the analyzed region, $\sum_i$ is summation over all atoms i in the analyzed region, and $\sum_j$ is summation over all atoms j except atom i ($\sum_k$ is summation over all atoms k except atom i and atom j). The u_{ij} and ϕ_i , of which U_T consists, are the binding energy between atom i and atom j and the energy of atom i itself, respectively. The u_{REPij} , u_{SHTij} , u_{IONij} , and u_{VDWij} , of which u_{ij} in turn consists, are repulsive energy, short range energy (including both covalent bond energy and metallic-bond energy), ionic bond energy, and van der Waals energy, respectively. The terms, $u_{REPij} + u_{SHTij}$, coincide perfectly with the original Tersoff potential in the case that there is no charge transfer. The e is the elementary charge, π is the circular constant, and ϵ_0 is the permittivity of the vacuum, r_{ij} is the distance between atom i and atom j , θ_{ijk} is the angle between bond ij and bond ik , and q_i is the charge of atom i , respectively.

The q_i is a variable which changes with time (like atomic coordinates do), and is recalculated at every time step so that U_T is minimized. As a result of this, the effects of charge transfer are taken into account in the changes of u_{IONij} , u_{SHTij} , and the other terms.

Parameter values for the Si, O, and H atoms are shown in Table 1⁽⁷⁾. These values were determined as

Table 1 Parameters of the interatomic potential function

atom	Si	O	H
$A (\times 10^{-18} \text{ J})$	293.33	533	13.99
$B (\times 10^{-18} \text{ J})$	75.491	41.8	6.34
$\lambda (\times 10^{10} / \text{m})$	2.4799	5.36	4.00
$\mu (\times 10^{10} / \text{m})$	1.7322	2.68	2.00
$\beta ()$	1.0999×10^{-6}	2.0	2.0
$n ()$	0.78734	1	1
$m ()$	3	1	1
$c ()$	1.0039×10^5	0	0
$d ()$	16.218	1	1
$h ()$	-0.59826	0	0
$R_s (\times 10^{-10} \text{ m})$	2.6	2.6	2.6
$S_s (\times 10^{-10} \text{ m})$	3.0	3.0	3.0
$R_L (\times 10^{-10} \text{ m})$	1.1	1.1	1.1
$S_L (\times 10^{-10} \text{ m})$	5.0	5.0	5.0
$I_E / e (\text{J/C})$	8.15	13.61	13.60
$A_E / e (\text{J/C})$	0.60	1.48	0.75
$Q_L / e ()$	-4	-2	-1
$Q_U / e ()$	4	6	1
$D_L (\times 10^{-10} \text{ m})$	1.62	1.48	2.26
$D_U (\times 10^{-10} \text{ m})$	-1.54	-1.12	-0.74
$n_B ()$	10	10	10
$\eta ()$	0.930	0.930	1.30
$C_{VDW} (\text{Jm}^6)$	0	0	0

follows.

First, parameters A through S_s in Table 1, are parameters which were in the original Tersoff potential, and are determined using the original ideas of Tersoff⁽⁶⁾. Next, I_E and A_E are the ionization energy and the electron affinity, respectively, of each atomic species, and are given in various Handbooks (e.g. Ref. (9)). D_U and D_L are the differences in atomic diameter between the neutral atom and the atom charged to the upper limit value Q_U and the lower limit value Q_L , respectively, and are determined easily from the Pauling's ionic radii⁽⁹⁾. The n_B is a parameter which controls the extent of the change caused by charge transfer on the depth of the short-range potential energy curve. The value used in this paper, 10, corresponds to an assumption that this depth change is small. C_{VDW} is a parameter which express the effects of the van der Waals force, and is assumed to be zero here. R_L and S_L are the inner and outer cut off radii of ionic bond energy, and are fixed so that calculated

ionic bond energy values coincide with the Madelung's energy value⁽¹¹⁾ (which is a rigorous value in the case where we assume that point charges with the formal charge values are positioned at the centers of the atoms in the SiO_2 crystal arrangement⁽¹⁰⁾). Finally, η is the ratio of the effective charge of the ionic bond energy to the real charge of the atom, and is introduced to take into account the effects of the distribution of electron charges. It is used as a final adjusting parameter.

2.2 Potential verification

In this section, to verify the proposed potential, material properties are calculated for various uniform bulk solids and gases, and the results are compared with experimentally obtained ones.

With conventional interatomic potentials it is difficult to reproduce the properties of multiple materials in a unified way, although properties of a single material are reproduced with no difficulty. Unified reproduction of the properties of multiple materials is necessary, however, for an interatomic potential to be usable in simulations of phenomena involving atmospheric influence, which implicitly includes reactions between different materials.

Important properties for verifying an interatomic potential are the interatomic bond length R_e , the lattice constants a , b , and c , the binding energy per atom U_a , and the elastic constants. Young's modulus, E , is one of the most important elastic constants in solids. On the other hand, the force constant, k , is more important for gas molecules, and corresponds to the spring constant of an interatomic bond in equilibrium state. These values are calculated for various materials consisting of O, H, and Si atoms, using the method in reference⁽¹²⁾.

The calculated results are shown compared with experimentally obtained ones⁽⁹⁾ in Tables 2 through 6, from which it is clear that the results coincide well. Table 7 shows that values obtained by the present calculation method coincide fairly well for the charges of Si and O atoms in SiO_2 with values obtained using quantum mechanics⁽¹³⁾.

With respect to the bond length R_e , of H_2O , and to the lattice constants a and c , of SiO_2 , however, calculated values were a bit different from experimental values. This is thought to be caused by the fact that the values used for D_L and D_U in this calculation were not strict. These values may be adjusted, and the degree of coincidence between calculated and experimental values may be thus improved. In this paper, however, Pauling's original ionic radius values were used unadjusted, to simplify parameter setting.

In Fig. 1, values of U_a taken from Tables 2 to 6 are compared among various materials. One can see

Table 2 Comparison of calculated values and experimental values⁽⁹⁾ of properties of O₂

	Calculated	Experimental
Re (pm)	120.9	120.8
U _a (aJ)	-0.410	-0.410
k (N/m)	1178	1177

Re: bond length

U_a: binding energy per atom

k: force constant

Table 3 Comparison of calculated values and experimental values⁽⁹⁾ of properties of O₃

	Calculated	Experimental
Re (pm)	133	128
U _a (aJ)	-0.329	-0.331

Table 4 Comparison of calculated values and experimental values⁽⁹⁾ of properties of H₂

	Calculated	Experimental
Re (pm)	74.2	74.1
U _a (aJ)	-0.359	-0.359
k (N/m)	575	575

Table 5 Comparison of calculated values and experimental values⁽⁹⁾ of properties of H₂O

	Calculated	Experimental
Re (pm)	122	96
U _a (aJ)	-0.507	-0.508

Table 6 Comparison of calculated values and experimental values⁽⁹⁾ of properties of SiO₂ (α quartz)

	Calculated	Experimental
a (pm)	548	491
c (pm)	623	540
U _a (aJ)	-0.855	-1.03
E _i (GPa)	80	78

a, c: Lattice constants

E_i: Young's modulus in <100> directionTable 7 Present calculation values and quantum mechanics values⁽¹³⁾ of charges of SiO₂ (aC)

	Present Cal.	Quantum Mech.
Si	0.344	0.384
O	-0.172	-0.192

that experimental values are uniformly reproduced by the present potential.

U_a (the binding energy per atom) is a very important index of stability for materials⁽⁶⁾. Materials which are not stable in the real world are falsely made to seem stable in simulations of systems which contain multiple species of atoms, if a potential is used in which the order relationship between the materials'

Fig. 1 Comparison of calculated values and experimental values⁽⁹⁾ of binding energy for different materials consisting of Si, O, and H atoms

U_a values does not coincide with the order of the real U_a values of the materials constructed from the atoms in the system.

Let us consider, for example, the order of the U_a values of H₂, O₂, and H₂O (Fig. 1). H₂O has the lowest value and, therefore, is the most stable. If charge transfer is not taken into account in the calculation, the U_a value of H₂O becomes the average of the values of H₂ and O₂, and this does not coincide with actual behavior. If we do take charge transfer into account, the U_a value of H₂O becomes lower than that of O₂. This is because ionic forces are added by transfer of charge from the H atoms to the O atoms in the H₂O. We can explain the reaction that produces H₂O from H₂ and O₂ as being due to this decrease in energy.

3. Calculation of Bond-Breaking Behavior

In this section, the influence of H₂O is calculated on the breaking behavior of the interatomic bonds in SiO₂, by using the interatomic potential explained in section 2. Section 3.1 and 3.2 gives the calculation model and the results, respectively.

3.1 The calculation model

Here, we make as a simple model as possible to quantify the qualitative model of interatomic bond-breaking behavior proposed by Michalske and Freiman⁽⁸⁾. Atoms are arranged near the tip of a crack in a piece of SiO₂, as shown in Fig. 2. One Si-O bond is focused at the tip of the crack. A basic model without the H₂O molecule is shown in Fig. 3(a), constructed by the atoms which are around this bond and have large influences on this bond. The modified model shown in Fig. 3(b) is constructed to calculate the influence of the H₂O molecule, which is added near the crack tip.

We calculate the force, F , acting through the focused Si-O bond as follows. The atoms below this

Fig. 2 Schematic atomic arrangement near a crack tip in SiO_2

Fig. 3 Initial atomic arrangements for the model of Si-O bond-breaking behavior: (a) without H_2O , and (b) with H_2O

Si-O bond are fixed. This bond is then elongated by displacing the atoms above this bond upward. The total energy U_T of the system is calculated at various elongation values, δ , of this bond. Force F is calculated by numerically differentiating U_T with respect to δ . The unit interval of elongation δ used for numerical calculations is 5 pm.

In the case where H_2O is present, calculation proceeds as follows. The focused Si-O bond is elongated from the initial atomic arrangement shown in Fig. 3(b). The position of the atoms in the H_2O are calculated repeatedly until they converge into a stable arrangement, while the positions of the atoms in the SiO_2 are temporarily fixed. At this point, U_T is calculated for this arrangement. This calculation is repeated at various values of δ in the elongation process. F is obtained based on these U_T values. Calculation is performed using the molecular dynamics method with the leapfrog scheme⁽⁵⁾ and a time interval 1.5 fs. Atomic velocity is damped by 20% at each time step to achieve convergence. The

Fig. 4 Changes in atomic arrangement during the Si-O bond elongation process in SiO_2 ((a) elongation $\delta = 0$, (b) $\delta = 70$ pm, and (c) $\delta = 400$ pm). In this figure the smallest, middle, and largest atoms are H, Si, and O atoms, respectively

Fig. 5 Effects of H_2O on the relationship between force and elongation (F - δ curve) of a Si-O bond in SiO_2

convergence judgment condition is that all atomic displacements are less than 0.001 pm from one iteration to the next.

3.2 Calculated results

Changes in atomic arrangements during the bond elongation process are shown in Fig. 4. H_2O is divided into H and OH. H is drawn toward the O of the Si-O bond, and OH is drawn toward the Si as the Si-O bond is elongated. This behavior coincides well with the behavior deduced by Michalske and Freiman⁽⁸⁾.

The relationship between force F and elongation δ , of the bond (hereafter this relation is called an F - δ curve) is shown in Fig. 5. This figure shows that the curve peaks abruptly at the maximum force level in the case with H_2O , and contrarily has a broad plateau there in the case without H_2O .

4. Crack Extension Behavior

In this section, the influence of H_2O on the crack extension behavior of SiO_2 is investigated, based on the shape of the F - δ curve obtained in section 3. This influence is explained qualitatively in section 4.1 and

quantitatively in section 4.2.

4.1 Qualitative explanation

The basic concept for a qualitative explanation of the relationship between the $F-\delta$ curve and crack extension behavior has already been presented by White et al.⁽¹⁴⁾. A bond at a crack tip is broken when it exceeds an energy barrier ΔU by the help of the random thermal vibration of bonded atoms. The crack extends at a certain speed due to successive bond breaking. Based on this idea of the rate theory, White et al. pointed out the following interesting relationship:

The energy barrier height ΔU corresponds to the area of the region between the $F-\delta$ curve expressing bond character and a horizontal line with height F expressing the external force in the $F-\delta$ plane (Fig. 6). From this relationship, we find that the shape of the $F-\delta$ curve near the point of the maximum force $F_{\max}$ is the most important factor in determining the crack extension behavior. Applying this relationship to the $F-\delta$ curves obtained in the previous section 3, we arrive at the following results:

In the case without H_2O (Fig. 5), the shape of the $F-\delta$ curve near the maximum force point is broad. Therefore, ΔU increases suddenly when F becomes smaller than $F_{\max}$. As a result, crack velocity becomes very small. Contrarily, in the case with H_2O , the peak shape is sharp. Therefore, ΔU increases very slowly when F becomes smaller than $F_{\max}$. As a result, crack velocity does not become so small. Crack extends on and on, even if F is considerably smaller than $F_{\max}$. These results coincide well with experimental observations.

4.2 Quantitative calculation

In this section, quantitative calculation is performed based on the ideas in section 4.1 above.

Fig. 6 Relationship between the shape of the $F-\delta$ curve and energy barrier height for bond breaking ΔU

A quantitative analysis of crack extension behavior based on the rate theory has already been proposed by Sinclair⁽¹⁵⁾. Sinclair developed a detailed analysis method and used it to investigate cracks in Si. His analysis is rather complicated, however, and does not take atmospheric influence into account. Moreover, he did not compare his calculations with experimentally obtained results.

In this section, atmospheric influence is taken into account by using the idea of the previous section 4.1. We will introduce equations kept as simple as possible, and investigate what degree of coincidence is obtained.

At first, the shape of the $F-\delta$ curve near the $F_{\max}$ point is approximated by

$$\Delta\delta = C \cdot \Delta F^n, \quad (26)$$

where C and n are constants which express the shape of the curve. ΔF is the decrease of F from $F_{\max}$, expressed by

$$\Delta F = F_{\max} - F. \quad (27)$$

On the other hand, $\Delta\delta$ is the width of the $F-\delta$ curve at the force level F which is decreased by amount ΔF from $F_{\max}$ (See Fig. 6).

In this case, crack extension velocity is calculated as

$$v = a\nu_0 \exp \left\{ -C[(K_{Ic}^{1/m} - K_I^{1/m})F_0]^{1+n} / [(1+n)kT] \right\}, \quad (28)$$

where F_0 is a constant defined by

$$F_0 = \sigma_0 E^{-1/m} a^{2-1/(2m)} (2\pi)^{-1/(2m)} / [1 - 1/(2m)], \quad (29)$$

and m and σ_0 are constants which express the stress-strain ($\sigma-\epsilon$) behavior of the material and are related as in the following equation:

$$\epsilon = (\sigma/\sigma_0)^m. \quad (30)$$

The a is the distance between adjacent atomic bonds, E is the Young's modulus, T is the absolute temperature, k is the Boltzmann's constant, K_I is the stress intensity factor, K_{Ic} is the fracture toughness, and ν_0 is the fundamental frequency factor.

Equation (28) was obtained as follows. By breaking one atomic bond at the crack tip, the tip advances by the length a of an atomic bond distance. By repeating this process with frequency ν , crack velocity becomes

$$v = a\nu. \quad (31)$$

From the explanation according to the rate theory, frequency ν is

$$\nu = \nu_0 \exp [-\Delta U/(kT)], \quad (32)$$

where ΔU is the energy barrier height for bond breaking. From Fig. 6, ΔU is

$$\Delta U = \int_0^{\Delta F} (\Delta\delta) d(\Delta F). \quad (33)$$

By substituting Eq. (26) to the above equation, we find

$$\Delta U = C \cdot \Delta F^{1+n} / (1+n). \quad (34)$$

Fig. 7 Comparison between calculated results and experimental results⁽⁸⁾ of crack extension behavior in SiO_2

It is assumed that strain field near the crack tip is controlled by the stress intensity factor K_I , and that the nonlinear region of stress-strain behavior is produced only in the crack-tip region, with a relationship as expressed in Eq. (30). Based on these assumptions and Eq. (27), the relationship between ΔF and K_I is as follows:

$$\Delta F = (K_{Ic}^{1/m} - K_I^{1/m}) F_0. \quad (35)$$

In this equation, it is assumed that a classical, continuum-mechanics type strain field holds in the atomic level at the crack-tip region. It has been shown from atomic level analyses⁽¹⁶⁾ that this assumption works well in the case of perfectly brittle materials like SiO_2 .

Equation (28) is obtained by substituting Eqs. (32), (34), and (35) into Eq. (31).

Working from Fig. 5, the constants which express the shape of the F - δ curve are estimated at:

$$n = 0.1979, \quad (\text{in the case without H}_2\text{O}) \quad (36.a)$$

$$n = 0.874, \quad (\text{in the case with H}_2\text{O}) \quad (36.b)$$

$$C = 4.11 \times 10^{-9} [\text{m/N}^n], \quad (\text{in the case without H}_2\text{O}) \quad (37.a)$$

$$C = 1.323 \times 10^{-3} [\text{m/N}^n], \quad (\text{in the case with H}_2\text{O}) \quad (37.b)$$

Using these constants and $\alpha = 400 \times 10^{-12} [\text{m}]$, $\nu_0 = 10^{12} [1/\text{s}]$, $T = 300 [\text{K}]$, $K_{Ic} = 0.8 \times 10^6 [\text{Pa}\sqrt{\text{m}}]$, $m = 1$, and $\sigma_0 = E$, calculations were performed using Eq. (28), and the results are shown in Fig. 7 with together experimental data⁽⁸⁾.

We will focus on the K_I values at which crack velocity reaches a certain fixed value in Fig. 7. These values of K_I are strength values corresponding to these crack velocity values. Figure 7 shows that calculated strength values are a little bit lower than experimental ones. Concerning changes in the strength values from the case with H_2O to the case

without H_2O , and from the case with low crack velocity to the case with high crack velocity, however, the calculated values coincide well with the experimental ones.

5. Discussion

5.1 Change of F - δ curve-shape

It was shown in Fig. 5 in the previous section that the shape of the F - δ curve near its maximum is changed greatly by the presence of H_2O . In this section, the reason for this change is discussed.

The shape of F - δ curve is determined by the repulsive and attractive forces between atoms. Attractive forces contain both covalent bond forces and ionic bond forces, both of which are influenced by H_2O . Atomic arrangements give useful information about the mechanism of this influence.

Figure 4(b) is the atomic arrangement near the maximum force point (elongation $\delta = 70 \text{ pm}$) in the case with H_2O . This figure shows that one H atom separates from the H_2O , leaving OH, and come near to the O atom of the elongated Si-O bond. This can be explained as being due to the H, which has positive charge in H_2O , being attracted by the O, which has negative charge in the Si-O bond.

Now, we will discuss the bond forces between the Si and O atoms. The O atom of the Si-O bond has a negative charge and the Si atoms above and below it have positive charges. This O atom therefore attracts these Si atoms. This means that ionic bond forces are produced. When the H comes near the O, the positive charge of the H produces a force repulsive to the positively charged Si, and neutralizes the ionic-bond forces. As a result, the covalent bond forces, which are left, dominate. The ionic bond forces are long-range forces and change gradually with change in interatomic distance. Contrarily, covalent forces are short-range forces and change abruptly. This is thought to be the main reason why the shape of the F - δ curve changes to become sharp in the presence of H_2O .

5.2 Crack velocity

In Fig. 7 of the previous section, the calculated values of crack velocity are larger than the experimental ones. The reason is as follows. In the calculations, we used the energy value for breaking one atomic bond as the energy barrier value for extending a crack. In reality, however, patterns of deformation, in which multiple atomic bonds are elongated and broken at the same time, are needed to cause a crack to extend. As a result, the energy barrier value is thought to be larger than our calculated values. It is possible to take this situation into account by making a model which includes more atoms near the crack tip.

In this paper, however, a simple small-sized model was used to clarify the essence of the phenomenon.

The reason why the curve bends abruptly in the region below a crack velocity of 10^{-6} m/s in the experimental case without H₂O in Fig. 7, has been explained by Michalske and Freiman⁽⁸⁾, as follows: This experiment was conducted in N₂ gas. This gas contained a slight amount of H₂O. This H₂O was thought to cause the bending effect by diffusing to the crack tip when crack velocity is low.

6. Conclusions

The following results were obtained using an extended Tersoff interatomic potential in which interatomic charge-transfer effects are taken into account, and applying this potential to a static-fatigue strength analysis of SiO₂.

(1) It was shown that unified reproduction of various material properties of multiple compounds is possible using the extended Tersoff potential. This was demonstrated by comparison of calculated and experimental values of important properties of various materials consisting of Si, O, and H atoms.

(2) The mechanism of SiO₂ strength decrease due to H₂O was clarified, based on calculations using the extended Tersoff potential to investigate the behavior of the shape change of the F - δ curve due to H₂O (This curve express the relationship between the force, F , and elongation, δ , of an interatomic bond between Si and O atoms in SiO₂).

(3) Using a simple equation created to calculate macroscopic crack extension behavior from the atomic level F - δ curve, fair agreement was obtained between experimental and calculated results of the values of the strength decrease due to the presence of H₂O.

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