Molecular dynamics study of fracture accompanied by chemical reaction

Anton M. Krivtsov

akrivtsov@bk.ru

Abstract

A molecular dynamics model for fracture accompanied by chemical reaction is suggested. Crack initiation and development in specimens subjected to an uniaxial loading is considered. The oxidation of the initial and new specimen surfaces during the fracture process is taken into account. It is postulated that the material properties such as density, stiffness and strength are changing due to the oxidation. Influence of the chemical reaction (oxidation) on the fracture scenario is investigated. Fracture process for the specimens of different shape, with and without predefined defects is studied.

1 Introduction

Molecular dynamics is a powerful tool for modelling of fracture in material with various internal structure and defects distribution. In most of these models only single-phase material is considered. However in the real applications the fracture is closely connected with chemical reactions. In particular, for MEMS made from silicon the oxidation process accompanying the fracture is essential, since the mechanical properties if the silicon dioxide differs essentially from those of the pure silicon [1].

The following model is suggested. The properties of particles adjusting to the surfaces is changed mimicking the difference between the silicon and its dioxide: size of the particles became slightly bigger, the elastic and strength properties became substantially lower then for the initial particles. This change take place immediately and involves as the particles surrounding the original surfaces of the specimen, as the particles laying near the new surfaces provided by the fracture and crack development. Since the size of the particles increases, this can provide separation of the pieces of material — the oxidization induced fracture. In this case fracture and chemical reaction can stimulate each other resulting in a self-generating process. Although mainly we will be studying situations when the fracture is induces by an external load, the possibility and conditions of such self-generation will be considered.

2 Computational model

The simulation procedure applied in this work is similar to that used in [2, 3], in more details it is described in [4, 5]. The material is represented by a set of particles interacting through a pair potential $\Pi(r)$. The equations of particle motion have the form

$$m\ddot{\underline{r}}_k = \sum_{n=1}^{N} \frac{f(|r_k - r_n|)}{|r_k - r_n|}\left(\underline{r}_k - \underline{r}_n\right), \tag{1}$$

where $\underline{r}_k$ is the radius vector of the k-th particle, m is the particle mass, N is the total number of particles, and $f(r) = -\Pi'(r)$ is the interparticle interaction force. We use the following notation: a is the equilibrium distance between two particles ($f(a) = 0$), $D = |\Pi(a)|$ is binding energy, C is the stiffness of the interatomic bond in equilibrium, and T_0 is the period of vibrations of the mass m under the action of a linear force with stiffness C

$$C = -\Pi''(a) \equiv -f(a), \qquad T_0 = 2\pi\sqrt{m/C}. \tag{2}$$

We will use the quantities a and T_0 as microscopic distance and time scales. For a particle of mass m that is in equilibrium in the potential field $\Pi(r)$ its minimum velocity to reach infinity is $v_d = \sqrt{2D/m}$ — so called dissociation velocity. We will use this quantity as a velocity scale. To measure the level of thermal motion in material the velocities deviation Δv (mean-square value of random velocities) will be used. When Δv approaches dissociation velocity v_d then the thermal motion break the internal bonds in the material resulting in its melting.

Let us consider the classical Lennard–Jones potential:

$$\Pi_{LJ}(r) = D\left[\left(\frac{a}{r}\right)^{12} - 2\left(\frac{a}{r}\right)^{6}\right], \tag{3}$$

where D and a are the binding energy and the equilibrium interatomic distances, introduced earlier. The corresponding interaction force $f(r) = -\Pi'(r)$ has the form

$$f_{LJ}(r) = Q\left[\left(\frac{a}{r}\right)^{13} - \left(\frac{a}{r}\right)^{7}\right], \qquad Q \overset{\text{def}}{=} \frac{12D}{a}, \tag{4}$$

where Q is the interparticle force magnitude. In the case of the Lennard–Jones potential, the stiffness C and the binding energy D obey the relation $C = 72D/a^2$; the force (4) reaches its minimum value (the bond strength) at $r = b = \sqrt[6]{13/7}$, where b is the break distance. The corresponding break deformation of the Lennard–Jones bond is $\varepsilon_* = b - a \approx 0.109$. The Lennard–Jones potential is the simplest potential that allows one to take into account the general properties of interatomic interaction: repulsion of particles that approach each other, attraction of particles moving away from each other, and the absence of interaction at large distances between them. For calculations the shortened Lennard–Jones interaction will be used, given by formula

$$f(r) = \left[\begin{array}{ll} f_{LJ}(r), & 0 < r \leq b, \\ k(r)f_{LJ}(r), & b < r \leq a_{\text{cut}}; \end{array}\right. \tag{5}$$

where b is break distance for Lennard-Jones potential, a_{cut} is cut-off distance (for $r > a_{\text{cut}}$ the interaction vanishes). The coefficient $k(r)$ is the shape function

$$k(r) = \left[1 - \left(\frac{r^2 - b^2}{a_{\text{cut}}^2 - b^2} \right)^2 \right]^2 . \tag{6}$$

The cut-off distance will be set as $a_{\text{cut}} = 1.4a$, in this case only the first neighbors are interacting for the close-packed structures. For the general study of the fracture process this simplified potential is sufficient. If necessary the obtained results can be extended to more complex potentials describing the properties of materials more exactly.

In case of oxidation it is postulated that the properties of the particle is changing. The diameter and force magnitude for the oxidized particles will be denoted as $\tilde{a}$ and $\tilde{Q}$. For the silicon dioxide it approximately fulfills

$$\tilde{a}/a = 1.1 , \qquad \tilde{Q}/Q = 1/3. \tag{7}$$

The vector of interaction force between two original particles can be represented as following

$$\underline{f} = \Phi(r^2)\underline{r} , \qquad \Phi(r^2) \stackrel{\text{def}}{=} f(r)/r. \tag{8}$$

When one or both of the interacting particles are oxidized then the interaction law takes the form

$$\underline{f} = \Phi\left(\lambda(r^2 - \bar{a}^2) + a^2 \right) \underline{r} , \qquad \lambda \stackrel{\text{def}}{=} a^2/\bar{a}^2, \tag{9}$$

where function Φ is calculated using average values for the particle diameter and force magnitude:

$$\bar{a} \stackrel{\text{def}}{=} (a_1 + a_2)/2 , \qquad \overline{Q} \stackrel{\text{def}}{=} (Q_1 + Q_2)/2; \tag{10}$$

indexes 1 and 2 correspond to the first and the second interacting particle. The law (10) independently of the particles sizes preserve the same width of the potential well.

For simulation a two-dimensional material will be used, where particles are packed to form an ideal 2D close-packed (triangular) crystal lattice. This is simplified lattice, however its symmetry is same as the symmetry of [111] surfaces of 3D crystal lattices, such as FCC and diamond (the last one is the lattice of silicon crystals). For the computations periodic boundary conditions are applied at all boundaries. All specimens are subjected to uniaxial loading by applying a small uniform deformation to positions of all particles and to the periodic boundaries. After each step of deformation a step of MD computation is used. The deformation is changing according the formula

$$\varepsilon(t) = \varepsilon_{\text{max}} \frac{t}{t_{\text{max}}}, \tag{11}$$

where ε_{max} is the maximum value of strain, t_{max} is the time of computation. The strain is directed along one of the sides of triangles, forming the lattice. The computation parameters are given in the Table 1.

Parameter	Symbol	Value
Number of particles	N	10^5
Cut-off radius	a_{cut}	$1.4\,a$
Initial velocity deviation	Δv	$0.005\,v_d$
Integration step	Δt	$0.02\,T_0$
Maximum strain	$\varepsilon_{\max}$	0.15
Strain rate	$\varepsilon_{\max}/t_{\max}$	$0.002\,T_0{}^{-1}$
Chemical inflation	$\tilde{a}/a$	$1.10 \div 1.15$
Chemical strengthening	$\tilde{Q}/Q$	$1/3$

Table 1: Computation parameters.

3   Results of computations

The results of the first computer experiment are presented in Fig. 1. A single vacancy placed in the center of specimen is used to initiate a crack. In Fig. 1a no chemical reaction is taken into account. In this case four straight cracks are propagating in crystallographical directions. In Fig. 1b,c the particles adjusting to the crack surfaces are subjected to oxidation that results in change of particle size (chemical inflation) and bond strength. The bond strength for the oxidized material in all experiments is taken three times lower then for the original material. The chemical inflation is 10% for Fig. 1b and it is 15% for Fig. 1c, e.g. $\tilde{a}/a = 1.10$ and $\tilde{a}/a = 1.15$ respectively. In the figures the original material is shown by blue color, the oxide — by cyan, the empty space is white. From Fig. 1b it follows that oxidation stimulates the fracture: initial fracture zone appears in the vicinity of the initial vacancy, where the oxidized material forms an elliptical area; the cracks are producing branches, substantially complicating the crack shape. In Fig. 1c it is visible that when the chemical inflation is increased from 10% to 15% then the amount of the oxidized material is increased in many times. The explanation of this phenomenon is that the break extension of the interatomic bond for the considered interaction potential is 11%. If the chemical inflation rate is greater then this value, then the chemical reactions produces fracture in material. The fracture creates new surfaces, where oxidation takes place, again producing the fracture and so on. Thus we have self-developing process, where the chemical reaction and fracture stimulate each other. If the greater values of the chemical inflation are used then this process can take place without external loading at all, resulting in very fast oxidation of the whole specimen. Also the high chemical inflation can result in the crack closing, since the oxidized material requires more space then the original one. If the oxide would not be weaker then the original material then a self-healing of the material can be realized.

Fig. 2 shows the sequential stages of the fracture process for the specimen with circular hole. The chemical inflation is 10%. No predefined crack is used, the fracture starts just from the inner boundaries of the specimen. From the very beginning several cracks appear, then the branching process produces very complicated, fractal
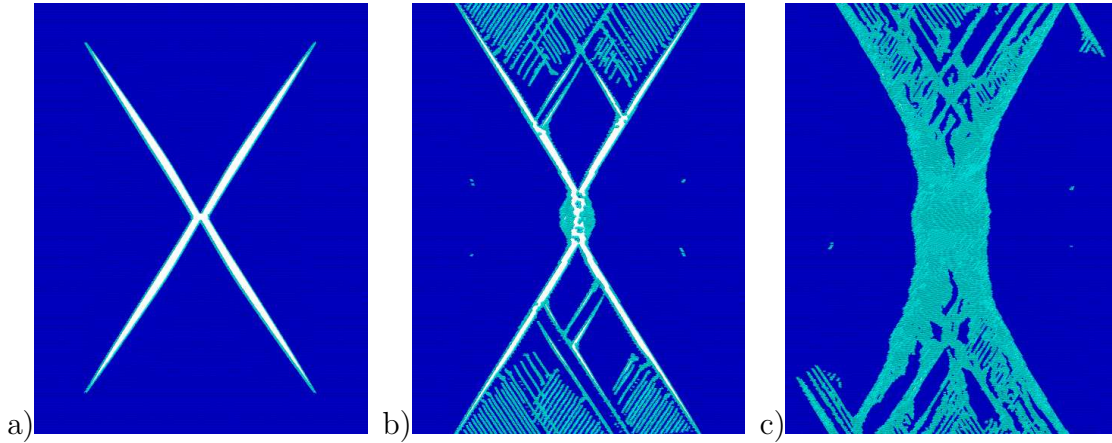
Figure 1: Comparison of the computational results for different rate of chemical inflation: a) no chemical reaction, b) 10% chemical inflation, b) 15% chemical inflation.

structure of the cracks. Zoom-up of the specimen with the developed crack is shown in Fig. 3.
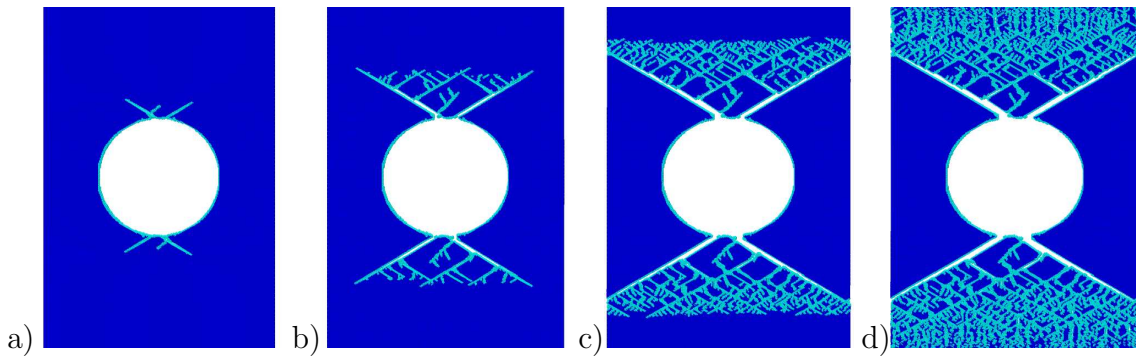

Figure 2: Sequential stages of extension for the specimen with circular hole: a) $\varepsilon = 7\%$, b) $\varepsilon = 10\%$, c) $\varepsilon = 13\%$, d) $\varepsilon = 15\%$.

Comparison with extension of the specimen with a predefined crack is shown in Fig. 4. Figure shows, that the predefined crack localizes the beginning of the fracture in the specified area, however the developed crack due to its branching does not depend much, whether the predefined crack was introduced or not.

Comparison of the results for the different rate of the chemical inflation is shown in Fig. 5. The specimen with a circular hole and predefined crack is used. As for the case of the fracture starting from a single vacancy, increasing the rate of the chemical inflation over the critical value of 11% results in abrupt increase of the oxidized area. The oxide is located not only in the vicinity of the crack, but also it is forming a wide belt around the hole, forming zone of plastic deformation.
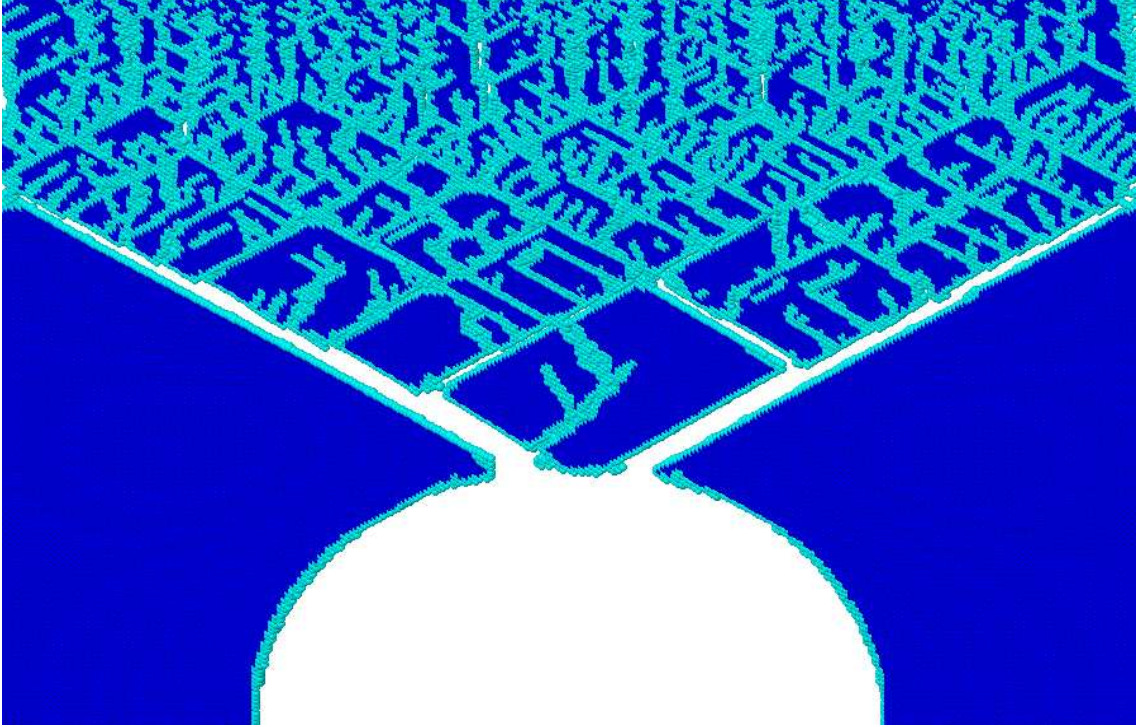
Figure 3: Zoom-up of the specimen with the developed crack, $\varepsilon = 15\%$.

4   Conclusions

A molecular dynamics model for the fracture accompanied by a chemical reaction was suggested. A crack initiation and development in specimens subjected to an uniaxial loading was considered. The oxidation of the initial and new specimen surfaces during the fracture process was taken into account. It was taken into account that the material properties such as density, stiffness and strength are changing due to the oxidation.

The results of the computer experiments show that oxidation stimulates the fracture. The cracks are producing branches, substantially complicating the crack shape. The branching of the cracks forms fractal-like structures: the longer is the fracture process the greater is the number of branches and subbranches.

If the rate of the chemical inflation is over the the break extension of the interatomic bond then an abrupt increase of the oxidized area can be observed. The explanation of this fact is that in this case the chemical reactions produces fracture in the material. The fracture creates new surfaces, where oxidation takes place, again producing the fracture and so on. Thus a self-generating process is realized, where the chemical reaction and fracture stimulate each other. For the greater values of the chemical inflation this process can take place without external loading at all, resulting in a very fast oxidation of the whole specimen. Also the high chemical inflation can result in the crack closing, since the oxidized material requires more space then the original one. If the oxide would not be weaker then the original material then the oxidation can result in a self-healing of the material.
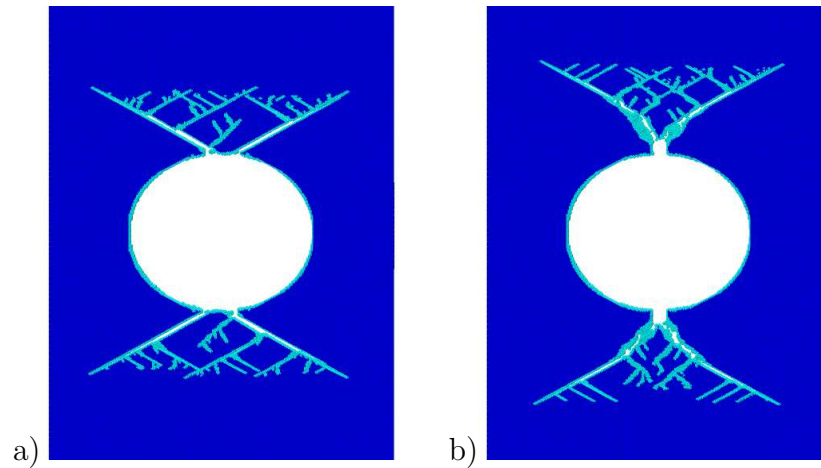
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Figure 4: Comparison of 10% extension for the specimen: a) without predefined crack, b) with predefined crack.
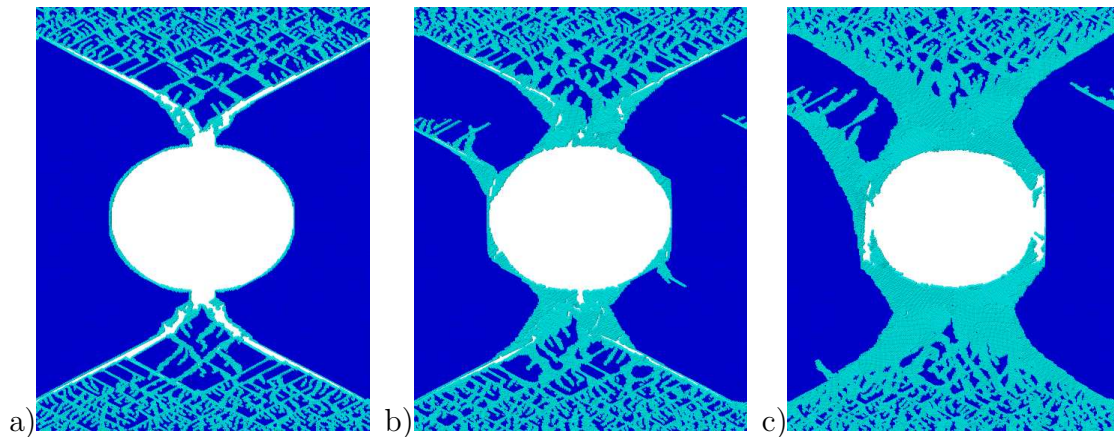

Figure 5: Comparison of results for different chemical inflation: a) 10%, b) 12%, b) 15%.

Acknowledgements

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Anton M. Krivtsov, Institute for Problems in Mechanical Engineering Russian Academy of Sciences, Bolshoy pr. V.O., 61, St. Petersburg, 199178, Russia.