

Dynamics of Consolidation and Crack Growth in Nanocluster-Assembled Amorphous Silicon Nitride

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Consolidation and fracture dynamics in nanophase amorphous Si_3N_4 are investigated using 10^6 -atom molecular-dynamics simulations. At a pressure of 15 GPa and 2000 K, the nanophase system is almost fully consolidated within a fraction of a nanosecond. The consolidation process is well-described by the classical theory of sintering. Under an applied strain the consolidated system develops several cracks which propagate parallel to each other, causing failure at multiple sites. The critical strain at which the nanophase system fractures is much larger than that for crystalline Si_3N_4 .

I. Introduction

NANOPHASE ceramics, prepared by synthesis and sintering of nanometer-size clusters, have spurred a great deal of research activity by virtue of their ductile behavior at relatively low temperatures. The basic issue drawing much of the attention is how^{1,2} ultrafine microstructures and porosity affect the mechanical behavior of nanophase ceramics. This issue has a great deal of practical importance, especially because an understanding of the dynamics of consolidation and fracture is essential to designing ceramics for specific applications.²

In this paper we investigate the dynamics of sintering and fracture in nanophase amorphous silicon nitride³ ($\alpha\text{-Si}_3\text{N}_4$) using large-scale molecular-dynamics (MD) simulations. (There is considerable interest in silicon nitride because of its high strength, light weight, high wear, and corrosion resistance,⁴ and the ability to withstand high temperatures.) At 2000 K and under an applied pressure of 15 GPa, nearly full consolidation is reached within a fraction of a nanosecond. Surprisingly, though, the time evolution of this rapid consolidation process is in excellent agreement with the classical theory of sintering. We have also investigated dynamic fracture in the consolidated nanophase system at room temperature. MD simulations reveal that the consolidated nanophase system can withstand a much higher value of the external strain than conventional $\alpha\text{-Si}_3\text{N}_4$. This is largely due to multiple crack formation in the nanophase $\alpha\text{-Si}_3\text{N}_4$. These cracks propagate parallel to each other, causing fracture at multiple sites. In contrast, the conventional $\alpha\text{-Si}_3\text{N}_4$ system undergoes cleavage fracture at room temperature.

The MD simulations reported in this paper are based on an

effective interatomic potential for Si_3N_4 which consists of two- and three-body terms:^{5,6} The two-body terms take into account steric repulsion between atoms, charge-dipole interaction due to the large electronic polarizability of nitrogen, and charge transfer between Si and N atoms through screened Coulomb interactions.⁷ The three-body terms include bond-bending and bond-stretching contributions due to the strong covalent bonding in the system. The validity of the effective potential is established by comparing the MD calculations with various experiments:^{4,8-11} (i) the MD results for the bond length and bond-angle distributions in crystalline Si_3N_4 are in excellent agreement with neutron scattering measurements;⁸ (ii) the positions and relative heights of the peaks in the static structure factor for $\alpha\text{-Si}_3\text{N}_4$ are also in good agreement with neutron scattering experiments;⁹ (iii) the phonon density-of-states and the temperature variation of the specific heat of crystalline Si_3N_4 are in excellent agreement with experiments;⁸ and (iv) the elastic moduli of crystalline $\alpha\text{-Si}_3\text{N}_4$ along different crystalline directions^{10,11} also agree very well with the MD results.

II. Dynamics of Consolidation

In the MD simulations, the initial configuration consists of 108 amorphous Si_3N_4 nanoclusters[‡] positioned randomly (also random orientations) in a cubic MD box of length 331.84 Å. The initial mass density of this 1,131,732-atom nanophase system was 1.03 g/cm³. This system was thermalized at zero pressure and 2000 K for 10 000 MD time steps using the constant-pressure MD method.¹³ (Periodic boundary conditions were applied, and the equation of motions was integrated with the reversible multiple time-scale algorithm¹⁴ using a time step of 2 fs.) The pressure was increased to 1 GPa and the system was thermalized at 2000 K for 10 000 steps. Subsequently the external pressure was increased to 5 GPa and the system was thermalized for 10 000 steps. We repeated this procedure to obtain well-thermalized systems at 8, 10, 12, and 15 GPa. The nanophase system at 15 GPa was cooled gradually to room temperature. Gradually the external pressure was decreased from 15 to 10, 10 to 5, 5 to 1, and finally to 0 GPa; at each pressure the system was thermalized for 5000 steps.

Figures 1(a) and (b) show snapshots of the nanophase Si_3N_4 systems under external pressures of 1 and 15 GPa, respectively. Evidently the nanophase system is well-consolidated at 15 GPa, whereas the system at 1 GPa has a large number of pores. We have examined the structure of the consolidated system by calculating (i) the Si-N bond length, (ii) the nearest-neighbor coordination of Si atoms, and (iii) the N-Si-N and Si-N-Si bond-angle distributions. The structure of the consolidated system is found to be very similar to that of bulk amorphous

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[‡]The value of the charge transfer used in the effective potential is consistent with the electronic-structure calculation based on the LCAO method; see Ref. 7.

[‡]Amorphous nanoclusters of diameter 56 Å containing 10 479 atoms each were obtained from well-thermalized bulk $\alpha\text{-Si}_3\text{N}_4$. The MD calculations for bulk amorphous Si_3N_4 are presented in Ref. 12.

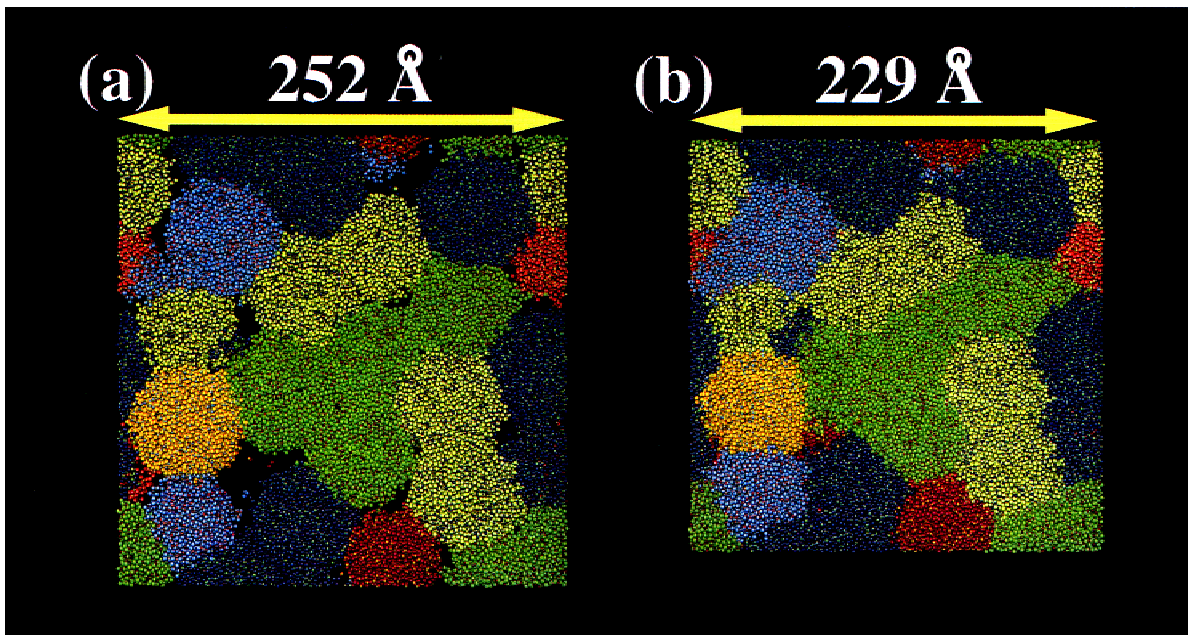


Fig. 1. Snapshots showing parts of 1,131,732-atom systems at external pressures of (a) 1 and (b) 15 GPa. Various colors are used to distinguish atoms of different nanoclusters.

Si_3N_4 .¹² The mass density of the final system, 3.09 g/cm^3 , is 97% of the experimental value of the density of crystalline Si_3N_4 (3.2 g/cm^3).

The dynamics of densification in nanophase amorphous Si_3N_4 is investigated at 2000 K. Figure 2 shows how the neck size between nanoclusters grows with time at a pressure of 15 GPa. The growth of neck radius is estimated from the average number of Si–N pairs (within 2.3 \AA distance) in the interfacial regions between nanoclusters. This time dependence of the average neck radius, x , can be fitted to

$$x = x_0 + At^\alpha \quad (1)$$

where x_0 is the initial value of x . We find that the best choice of the fitting parameters for the MD results is $A = 0.122$ and $\alpha = 0.203$. Thus the neck size between nanoclusters increases approximately as a one-fifth power of time. This result agrees with a sintering model based on volume diffusion.^{15,16}

The MD calculations for the mean-square displacement at

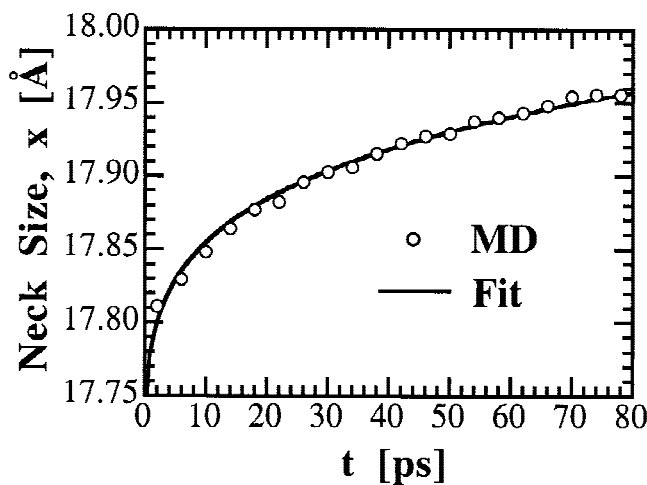


Fig. 2. Rate of the neck growth (x) in nanophase $\alpha\text{-Si}_3\text{N}_4$ under an external pressure of 15 GPa at 2000 K.

2000 K show that the self-diffusion constant of atoms near the neck regions is approximately $3.3 \times 10^{-6} \text{ cm}^2/\text{s}$. This indicates that within the time scale of an MD simulation ($\sim 100 \text{ ps}$) at 2000 K, an atom in the neck region travels across that region.

III. MD Simulation of Fracture

In the consolidated nanophase Si_3N_4 system, the growth of crack under the influence of an external strain is investigated. Periodic boundary conditions were removed in the fracture simulation. The system was first relaxed with the conjugate-gradient method,¹⁷ heated to 300 K, and after thermalization an external strain was applied (at the rate of 0.2% per picosecond) by displacing boundary-layer atoms in the x direction (those with x coordinates within 5.5 \AA thick layer near the boundaries). Each time the strain was increased by 1% and the system was relaxed for 20 ps. After the strain reached 5%, a notch of length 25 \AA along the y axis was inserted in the bottom layer of the x - z plane and then the system was further thermalized for 20 ps. Repeating this procedure of stretching and thermalization, we obtained several strained systems between 5% and 30%.

Figure 3 depicts crack surfaces and microvoids in four systems. (Microvoids are identified by dividing the system into voxels of length 4 \AA and then finding empty voxels; the material is not shown in this figure.) At 11% strain we find that the initial notch (yellow) begins to propagate and concomitantly microvoids are formed ahead of the crack tip. At a strain of 15%, the primary crack advances by coalescing with microvoids that lie ahead of the primary crack. As the strain is further increased (21%), secondary (magenta) and tertiary (white) cracks develop parallel to the primary crack and they also grow by merging with microvoids. Finally at a strain of 30% the primary and secondary cracks propagate through the material. [At this critical strain we also find another crack parallel to the primary and secondary cracks, near the right edge in Fig. 3(d).] These multiple cracks occur mainly in the intercluster regions.

Figure 4 shows the surface area of cracks in the nanophase and crystalline $\alpha\text{-Si}_3\text{N}_4$ systems. (Both systems have the same size and geometry.) When the strain on the nanophase system exceeds 10%, the total surface area of cracks begins to increase dramatically as the primary crack advances and microvoids are

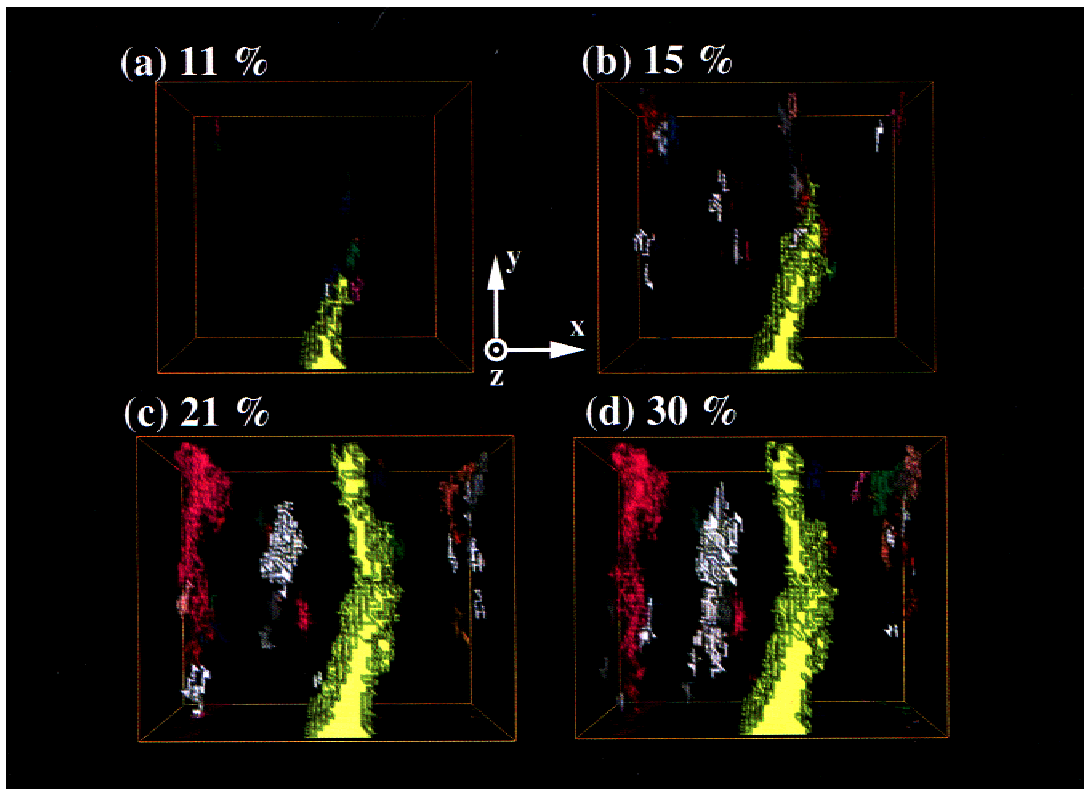


Fig. 3. Snapshots of crack surfaces with large ($>0.64 \text{ nm}^3$) microvoids. Applied strains are (a) 11%, (b) 15%, (c) 21%, and (d) 30%. The primary, secondary, and tertiary cracks are shown in yellow, magenta, and white, respectively. Microvoids are shown in different colors.

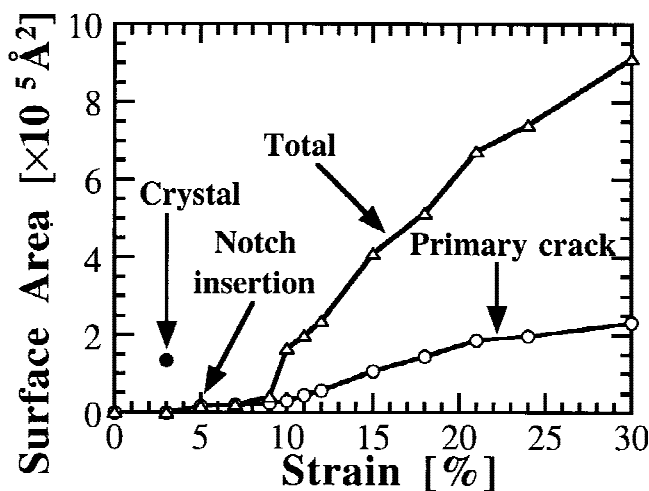


Fig. 4. Surface areas of the primary crack (open circles) and of all the cracks (open triangles) as a function of the external strain. Solid circle displays the result for crystalline $\alpha\text{-Si}_3\text{N}_4$ under a strain of 3%. The solid lines are drawn to guide the eye.

formed in the system [see also Fig. 3(a)]. Since the surface area of the primary crack grows gently with an increase in the applied strain, the large increase in the total surface area is caused by multiple crack formation. At the critical strain (30%) the total area of the fracture surface is 7 times larger than the crack surface area in the crystalline system. (The crystalline Si_3N_4 undergoes cleavagelike fracture at a strain 3%.)

IV. Effect of Multiple Cracks on Toughness

The effect of multiple cracks on the toughness of nanophase Si_3N_4 has been estimated from the fracture energy per unit area

(or crack-resistance energy¹⁸). The fracture energy was obtained from the MD simulation for the stress-strain relation. At the critical strain of 30% the fracture energy per unit area for the nanophase system is estimated to be 40 J/m^2 ; in contrast, its value for crystalline Si_3N_4 is only 4 J/m^2 . This comparison along with the analysis of fracture surfaces discussed in the preceding paragraph indicates that multiple cracks are primarily responsible for energy dissipation^{18–20} in the nanophase $\alpha\text{-Si}_3\text{N}_4$ system. This is consistent with a model calculation by Hoagland and Embury²¹ for the elastic interaction between microcracks around the main crack tip.

V. Conclusion

In conclusion, large-scale MD simulations reveal that the dynamics of densification in nanophase amorphous Si_3N_4 is well-described by the macroscopic theory of sintering based on volume diffusion. In consolidated nanophase amorphous Si_3N_4 , fracture occurs at multiple sites when several cracks propagate parallel to the primary crack in the system. This behavior is very different from that observed in a conventional amorphous Si_3N_4 film⁸ where fracture is caused by the propagation of a single crack coalescing with microvoids.

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⁸In an $\alpha\text{-Si}_3\text{N}_4$ film (see Ref. 10), only a single crack propagates and the fracture energy for the film is estimated to be 45% of the energy required to fracture the nanophase system. (The lateral size of the film is the same as that of the nanophase system.)

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