Tight-binding simulations of precipitation and growth of diamond from molten carbon under extreme pressure.

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Diamond is thermodynamically unstable at atmospheric pressure, the stable allotrope of carbon being graphite with a high potential barrier that separates graphite (sp^2 hybridized) from diamond (sp^3 hybridized). High pressure and high temperature must be applied in order to permit diamond crystal growth [1]. In 1961, small diamond crystallites were grown directly from graphite by shock compression during an explosion that created a high pressure of about 35 GPa and a temperature about 770 °C [2] lasting for a few microseconds. This technique of diamond nucleation is characterized by very fast quenching of the compressed gaseous carbon phase during expansion. The hexagonal form of diamond (lonsdaleite) has been found in meteorites and fabricated in the laboratory by applying uniaxial pressure to molten carbon [3]. In this study we simulate the fast quenching of a compressed (hydrostatically and uniaxially) molten carbon sample, followed by volume expansion. The goal of this research is to study the influence of the initial pressure (density) and cooling rates on the formation of diamond nanocrystallites in a manner that resembles the carbon phases produced during explosion.

The method used is tight-binding molecular dynamics [4] using the OXON package [5]. Here the electron wave functions are expanded in terms of a basis set of valence electron wave functions, controlling the attractive part of the potential, while the repulsive one is treated empirically. Color vizualization with the Atomic Vizualization package (AViz) [6] helped to identify the crystalline clusters (diamond or graphite) formed inside the amorphous carbon network.

The simulations were carried out at different densities (3.3, 3.5, 3.7, 3.9 and 4.1 g/cc) and cooling rates (200, 500 and 1000 K/ps). Some samples were compressed homogeneously in all three direction, whereas others were

compressed in one direction only. The samples thus generated were predominantly amorphous carbon (see Fig.1), containing diamond or graphite crystallites depending on cooling rate. For rapid cooling rates (1000 K/ps) predominantly sp^3 bonded clusters (see Fig.2) were formed. These clusters were characterized by computing the radial and angular distribution functions, which were found to be close to those of perfect cubic diamond at the same density. The band gap inside the diamond crystallites was found to be slightly narrower than that of perfect cubic diamond. At slower cooling rates (200 K/ps) graphitic clusters were formed. It is interesting that the application of uniaxial pressure does not lead to the formation of clear lonsdaleite crystallites, but as described above all samples appeared to be diamond. It should however be noted that that the differences between lonsdaleite and cubic diamond are small.

In spite of the fact that precipitation of diamond clusters inside an amorphous network is a random process some trends can be deduced from the simulations. The first is that the probability of precipitation of diamond crystallites increases with density. The second is that the probability of diamond precipitation increases as the cooling rate increases. At slower cooling rates some samples transform to graphite (Fig.3). These trends are in qualitative agreement with experimental results of detonation diamond nucleation [7], where increasing pressure (density) and cooling rates leads to a higher diamond fraction in detonation soot. In contrast, the probability of transformation to graphite decreases with cooling rate. In the cases when the samples were compressed in one direction, the orientation of graphitic planes is parallel to the direction of compression. If compression is homogeneous in all three direction then the orientation of the graphitic planes is random.

References

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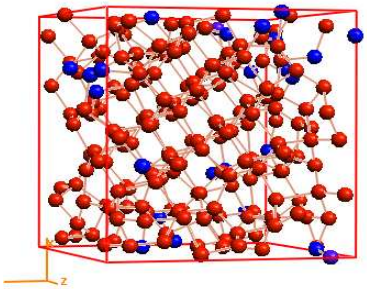

Figure 1: The structure generated at 3.9 g/cc (red balls are sp^3 coordinated atoms, blue balls are sp^2 coordinated atoms).

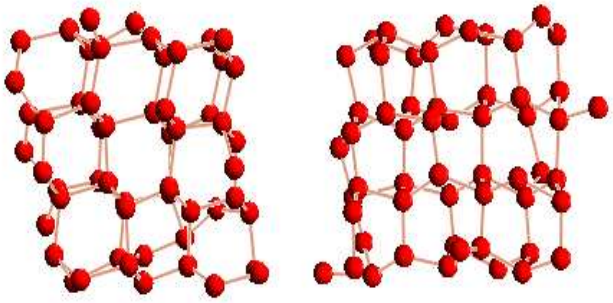

Figure 2: Diamond cluster inside an amorphous carbon network generated at 3.9 g/cc viewed from different directions.

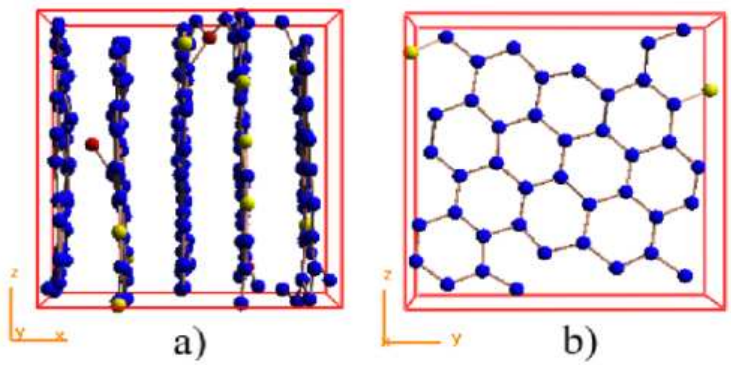

Figure 3: Graphitic configuration generated at 3.7 g/cc with intermediate cooling rate (500 K/ps) a) viewed from the direction parallel to the graphitic planes, b) one graphitic plane, viewed from the perpendicular direction.

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