

Nanodiamond stability with friction and heat

J Butterworth, K Briston, F Claeysens and B J Inkson

¹NanoLAB Centre, Department of Materials Science and Engineering, University of Sheffield, Sheffield, UK

E-mail: beverley.inkson@sheffield.ac.uk

Abstract. The structural stability of nanodiamonds (ND) has been investigated as a function of abrasion/friction and thermal annealing. Nanodiamonds examined before and after abrasion by transmission electron microscopy (TEM) are found to have modified surface characteristics. Frictional rubbing generates smaller, non-spherical particles with rougher, cleaner surfaces, and debris consisting of compacted ND+amorphous carbons. Annealing of ND and abraded ND at 1000°C demonstrates that abrasive pre-treatment increases proportion of transformation to onion-like-carbon (OLC) structures with generation of 3-30nm diameter OLC. The OLC achieved are of similar dimensions to those grown from ND annealed with a Ni catalyst but with more defective microstructures.

1. Introduction

Nanodiamonds (ND) can be fabricated by a number of methods including CVD, mechanical breakdown of bulk diamond and shock synthesis, with the latter method giving access to industrial scale manufacture [1]. Nanodiamonds have high hardness, strength and wear resistance, which together with their biocompatibility and distinctive optical properties gives rise to applications as polishing materials, lubricants, strong composites and potential as biomedical agents. Detonation nanodiamonds manufactured by shock synthesis are typically in the form of aggregations of ND nanoparticles, with cores of strongly bonded particles [1,2]. Aggregation, and mixed surface sp^n/sp^3 bonding, alters nanodiamond properties from bulk diamond.

Here the structural stability of detonation nanodiamonds has been investigated as a function of abrasion/friction and annealing at 1000°C. Detonation ND typically have their surface bonds terminated by graphitic or amorphous carbon and a range of stabilizing (C,H,O,N) functional groups [1,3]. These surface groups can allow the tailoring of nanodiamonds for a range of purposes such as drug delivery, but these stabilizing groups can also prevent graphitization and inhibit ND transformations [3]. The surface of diamond, and its termination by graphitic or amorphous carbon, may be modified by a range of methods including heat and mechanical shear [3-8]. Here the modification of ND by frictional abrasion has been investigated. Samples of ND are characterised by TEM before and after abrasion, and are found to have modified surface characteristics. Thermal annealing at 1000°C has been carried out to investigate the effect of abrasion on the ND-to-onion-like-carbon (OLC) transformation [4-6].

2. Abrasive stability of nanodiamond

Detonation nanodiamonds (NanoDiamond Products, Ireland) consisting of ~10nm diameter primary particles agglomerated in clusters (figure 1) have been subjected to abrasive wear tests and annealing, followed by TEM characterisation. ND in distilled water were dispersed ultrasonically before 50µl being dispersed onto a clean alumina sheet and dried. Abrasive testing between alumina counterfaces was carried out for 30 and 60min using a Buehler Minimet rotary polisher, 50rpm, F=98N. Abrasive debris was retrieved from the upper alumina platten by ultrasonic agitation in distilled water, and samples dispersed onto holey carbon grids for TEM (JEOL 2010F).



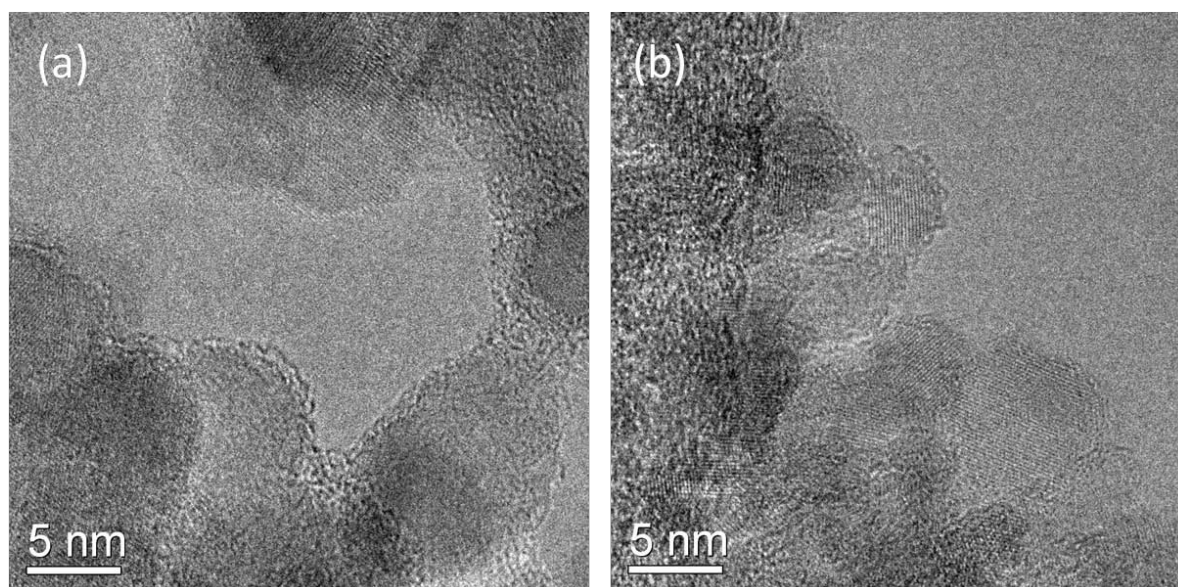


Figure 1. TEM images of nanodiamond particles. (a) As-received nanodiamond cluster with 5-10nm primary diamond particles enveloped in ~1nm of amorphous hydrocarbons. (b) 30 min abraded ND cluster.

As-received crystalline ND particles were typically 5-10nm in diameter, enveloped in ~1nm of amorphous hydrocarbons (figure 1a), and aggregated as clusters typical of detonation diamond [1-3]. The abrasive testing causes impacts between the ND clusters, and between ND clusters and the alumina substrate. Examination of the ND clusters after abrasion reveals that many have a significant reduction in the amorphous carbon layer observed on the as-received material. This is consistent with abrasion of the softer outer hydrocarbons and functional groups against other diamonds and the alumina plattens. It is also likely that there is local frictional heating during abrasion which may lead to loss of more volatile components. Frictional rubbing also generates smaller, non-spherical ND particles <5nm with rougher cleaner surfaces (figure 1b), which can originate from diamond-on-diamond wear. Some amorphous wear debris was also observed compacted with nanodiamond clusters. No evidence of graphitic or onion-like carbons was observed under these experimental conditions.

3. Thermal stability of abraded ND

ND are known to transform to onion like carbon (OLC) with thermal annealing [4]. Here samples of as-received ND and abraded ND were annealed at a temperature of 1000°C for 3 hours in vacuum furnace. This condition was chosen to ensure that the ND to OLC transformation would be in an early stage with partial ND→OLC transformation [4] to investigate whether abrasion affects the transformation rate. Additional as-received ND was also annealed mixed with Ni nanoparticles (20nm diameter), as Ni is a known catalyst for carbon graphitization transformations. The ND and Ni were mixed ultrasonically in a ND: Ni ratio of 75:25wt% before drying prior to the annealing treatment.

3.1. Thermal stability of nanodiamond

Figure 2 shows examples of the microstructure observed for as-received ND and abraded ND after vacuum annealing at 1000°C for 3 hours. The as-received ND demonstrated the initial stages of the diamond to OLC transition, with graphitic layers visible on the surfaces of clusters. In some cases closed concentric graphite shells could be observed completely enveloping small diamonds (figure 2b). The partial covering of ND in a few graphitic layers at 1000°C is consistent with the ordering of

carbon atoms on the surfaces of individual ND once surface groups (C,H,N,O) have thermally decomposed [4].

The annealed abraded diamond exhibited a distinctly different microstructure to the purely annealed ND. In addition to the growth of graphite on the diamond particles (figures 2a,b), a distribution of onion-like carbon balls 3-30nm in diameter (figures 2c,d) were observed throughout the annealed material. Figure 2d illustrates the structure of one of the larger OLC balls, which exhibit concentric but defective graphitic layering. These OLC originate principally from the amorphous hydrocarbon wear debris generated by the wear of the original ND surfaces, but also from complete transformation of the smallest diamond wear fragments.

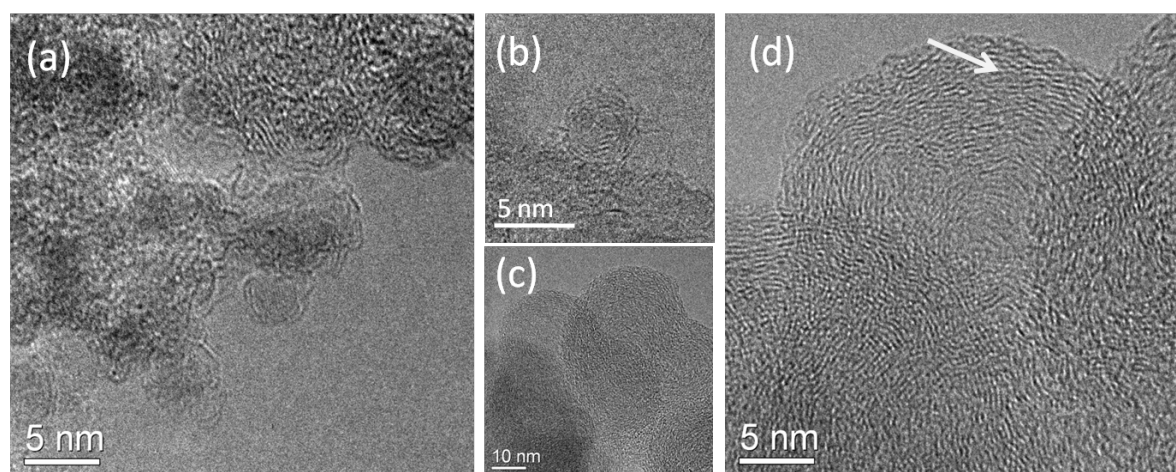


Figure 2. ND samples annealed at 1000°C for 3 hours. (a,b) As-received ND grows 1-3 layer graphite shells on diamond cores. (c,d) 30 min abraded ND annealing leads to growth of 3-30nm diameter OLC with defective graphite ordering (arrowed) from ND and amorphous carbon wear debris.

3.2. Thermal stability of nanodiamond+Ni nanoparticles

Figure 3 shows the microstructure observed for as-received ND annealed with Ni nanoparticles at 1000°C for 3 hours. The as-received ND annealed mixed with 25wt% Ni nanoparticles exhibited more conversion to graphite and OLC than purely annealed ND (figure 2a). ND particles were observed with well developed concentric shells of graphitic carbon, and graphitic sheets up to 10nm thick were also observed to envelop some Ni particles (figure 3a), indicating active diffusion of carbon and Ni throughout the sample. OLC of 2-25nm diameter were also observed, exhibiting very well ordered complete concentric graphite layers (figure 3b).

4. Discussion

Nanodiamonds have a range of potential uses exploiting the intrinsic properties of the diamond structure, however their high ratio of mixed sp^2/sp^3 surface bonding means that their activity is distinct from bulk diamond. Here abrasive wear of ND by collisions with other ND clusters and alumina counterfaces was observed to reduce the thickness of the surface hydrocarbons/functional groups, roughen the nanoparticle surfaces, and generate amorphous wear debris which compacted with the nanodiamond clusters. Under the abrasive conditions used, frictional shear/heating was insufficient to lead to graphitic debris, which has been observed *in situ* with single point contact shear of amorphous carbon [9].

Heating the detonation ND to 1000°C for 3 hours was sufficient to initiate the first stages of the diamond to graphite transformation, with onion-like shells of graphite growing around the ND particles [4]. The annealing of abraded ND however was quite different, revealing a highly accelerated transformation rate to OLC (figure 2c). Both small (<5nm) and large (>20nm) carbon

onions grow, with large amounts of disorder in the concentric graphite shells. The abrasive process reduces the amorphous layer on the ND (mechanical displacement and frictional heating), causes wear of the ND surfaces (exposing active surface sites), and generates 3rd body amorphous wear debris; all of which enable enhanced carbon diffusion and growth of graphitic carbon during the subsequent annealing process.

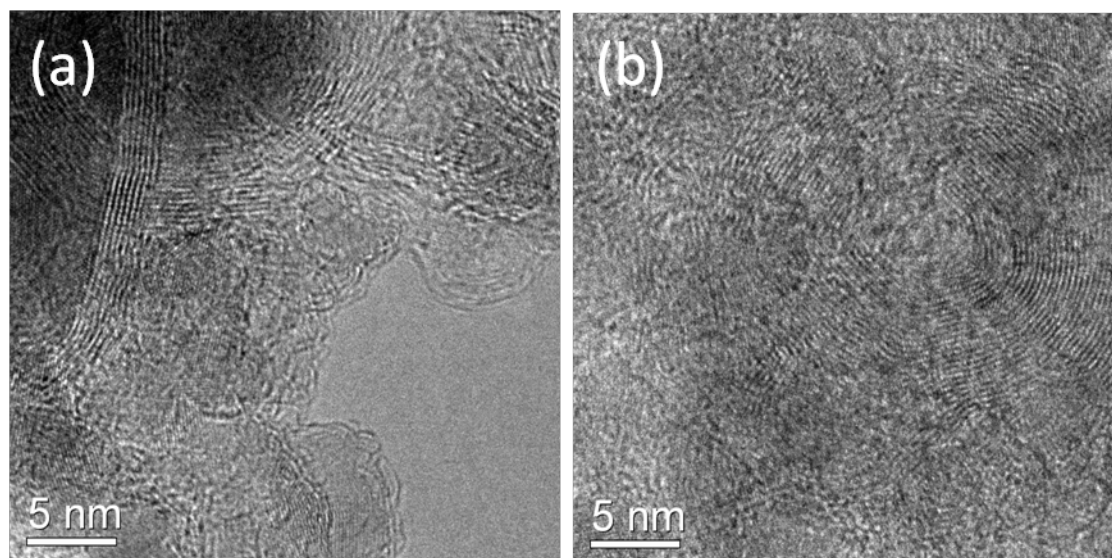


Figure 3. As-received ND+Ni nanoparticle sample annealed at 1000°C for 3 hours.
(a) Graphitization of the ND and Ni surfaces. (b) Growth of a highly ordered OLC sphere.

The role of friction and mechanical wear of ND clusters in accelerating the transformation rate of ND to OLC (figure 2), was compared to the use of catalyst Ni nanoparticles which also demonstrated increased transformation rate of ND to OLC (figure 3). Under the same thermal treatment (1000°C for 3 hours) OLC of similar dimensions were observed for both the abraded ND, and the ND+Ni mixture. The OLC generated from the abraded ND however had highly defective graphitic ordering, compared to the high-quality OLC with concentric graphite shells grown in the presence of diffusing Ni.

References

- [1] Mochalin V N, Shenderova O, Ho D and Gogotsi Y 2012 *Nature Nanotech.* **7** 11
- [2] Krüger A, Kataoka F, Ozawa M, Fujino T, Suzuki Y, Aleksenskii A E, Ya. Vul' A and Ōsawa E 2005 *Carbon* **43** 8 1722
- [3] Kuznetsov V L and Butenko Y V 2005 *Synthesis, Properties and Applications of Ultrananocrystalline Diamond*, ed D M Gruen *et al* (Netherlands: Springer Press) p 199
- [4] Kuznetsov V L, Chuvilin A L, Butenko Y V, Mal'kov I Y and Titov V M 1994 *Chem. Phys. Lett.* **222** 4 343
- [5] Aleksenskii A E, Baidakova M V, Vul A, Davydov V Y and Pevtsova Y A 1997 *Phys. Solid State* **39** 1007
- [6] Chen J, Deng S Z, Chen J, Yu Z X and Xu N S 1999 *Appl. Phys. Lett.* **74** 3651
- [7] Butenko Y V, Kuznetsov V L, Churilin A L, Stankus S V, Khaitulin R A and Sagall B 2000 *J. Appl. Phys.* **88** 4380
- [8] Pastewka L, Moser S, Gumbsch P and Moseler M 2011 *Nature Materials* **10** 34
- [9] Wang J J, Lockwood A J, Peng Y, Xu X, Bobji M S and Inkson B J 2009 *Nanotechnology* **20** 305703