When diamonds are not pure diamond: amorphous carbon (a-C) grain boundary complexions in natural diamond aggregates

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Introduction

Detailed scanning electron microscope (SEM) imaging of tens of thousands of natural diamonds has revealed many characteristics that were previously unobserved with optical microscopy. One of these is a distinct variation in the grain boundary characteristics of natural diamond aggregates. Under SEM imaging, adjoining crystals in a diamond aggregate may appear poorly welded or, alternatively, may appear well fused (Figure 1), with this variation often linked to specific diamond populations. To determine the cause of this variation, grain boundary complexions from a selection of poorly welded and well fused natural diamond aggregates were characterised using a combination of electron backscatter diffraction (EBSD), bright field (BF) and low angle annular dark field (LAADF) scanning transmission electron microscopy (STEM), electron dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS) at the GrainBound LLC laboratory in Pennsylvania, USA.
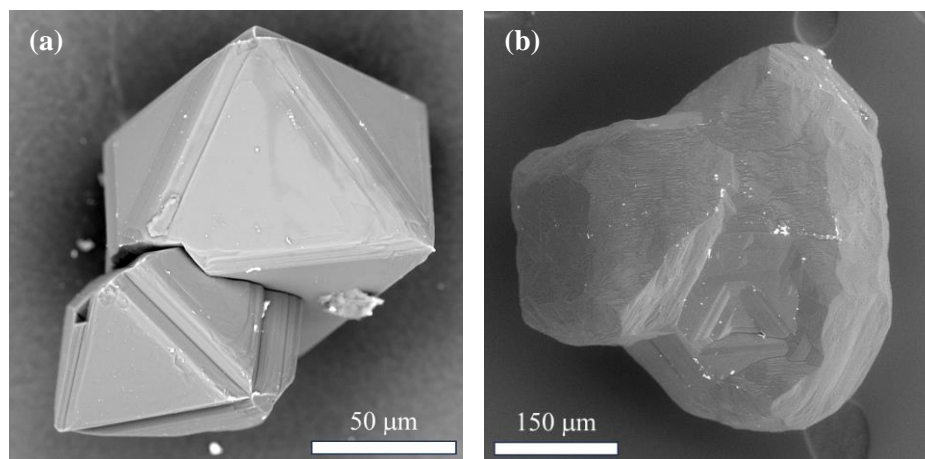

Figure 1: Backscatter electron SEM images of (a) poorly welded and (b) well fused crystals in natural microdiamond aggregates.

Grain boundary complexions consist of interfacial material that is in thermodynamic equilibrium with the abutting phase(s) and has a stable, finite thickness that is typically on the order of 0.2–2 nm (Cantwell et al., 2014). As described in Cantwell et al. (2014), a complexion cannot exist independently of the abutting phases and its average composition and structure need not be the same as the abutting phases. Complexions exhibit phase-like behaviour and transform in response to changes in thermodynamic parameters. Grain boundary complexion transitions are difficult to predict a priori and typically occur independently of bulk

phase transformations (i.e., at different values of temperature, pressure, or composition). They have not previously been identified in natural diamonds.

Analytical Results

Analysis of the natural diamond aggregate samples reveals that well fused aggregates are characterised by clean complexions between adjacent σ∗ bonded diamond crystals that are structurally abrupt and not detectably widened. In contrast, diamond aggregates with a poorly welded appearance have grain boundary complexions characterised by the transformation of σ∗ bonded diamond into ~1 nm thick amorphous carbon (a-C) films with π∗ bonding (Figure 2). While graphite also contains π∗ bonds, the absence of any coherent atomic structure or layering within the grain boundary complexion interfacial material excludes the option of transformation to graphite as the causative of the π* bonds.
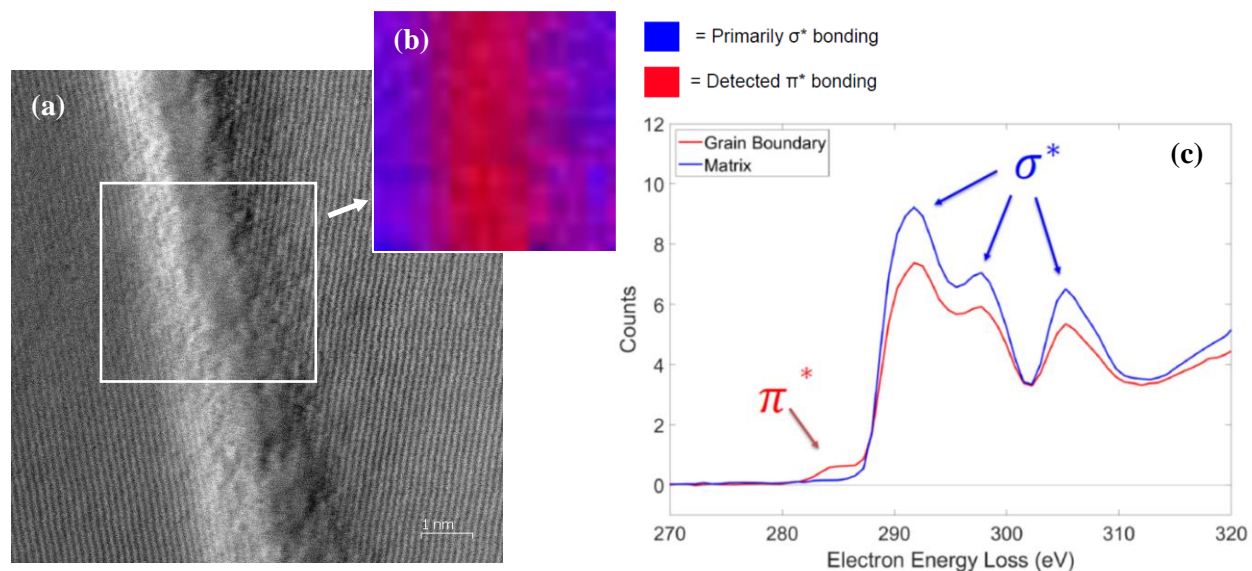

Figure 2: (a) Atomic-resolution STEM image of a 1.45 nm wide grain boundary complexion between two adjacent diamond crystals in a poorly welded natural aggregate. The absence of any coherent atomic structure or layering within the grain boundary complexion interfacial material indicates this is an amorphous film. (b) Colour-coded map showing distribution of σ* and π* bonds across the grain boundary complexion. (c) Examples of diamond matrix and grain boundary complexion EELS spectra used to map the distribution of σ* and π* bonds. The shoulder at 285 eV in the grain boundary spectrum is indicative of π* bonding. Due to the inclined orientation and/or narrow geometry of the grain boundary complexion interfacial material, diamond peaks are unavoidably detected in the grain boundary EELS spectrum, resulting in a mixed signature that cannot be used to distinguish the a-C from graphite.

Amorphous carbon is a non-crystalline solid allotropic form of carbon (Kouchi, 2011). While some short-range order may be observed, there is characteristically no long-range pattern in the positions of the carbon atoms. Amorphous carbon has localized π electrons and its bonds form with lengths and distances that are inconsistent with any other allotrope of carbon.

Grain Boundary Complexion Transformation

The presence of a-C films along the grain boundaries in poorly welded diamond aggregates suggests they have undergone the equivalent of a premelting complexion transformation. Premelting refers to the transformation of an interface into a disordered layer that forms a film on a crystalline surface (or at a grain boundary, phase boundary or free surface) at a temperature below the bulk melting temperature or solidus

of the underlying crystal, in response to changing thermodynamic conditions (Cantwell et al., 2014). Extensive further research and experimental studies would be required to determine the exact thermodynamic conditions responsible for the diamond grain boundary complexion transformations, which would have taken place at temperatures substantially lower than the $> 4000\ ^{\circ}$C bulk melting temperature of diamond (refer to Ghiringhelli et al., 2005, Figure 1, for a reference carbon phase diagram). Possible directions for such research might be hinted at by the experimental results of O'Bannon et al. (2020), who reported the presence of an a-C phase generated during experiments on diamond-to-graphite transformation at $P = 1$ GPa and $T = 1300\ ^{\circ}$C, in the presence of an H_2O fluid. They did not provide much detail on the a-C – their publication instead focused on a co-occurring unusual linear carbon phase – but they did identify it as one of the intermediary phases generated during multi-stage transformation of diamond to graphite.

As a result of grain boundary complexion transformation, the poorly welded aggregates are no longer pure diamond sensu stricto. They are instead a hybrid material consisting of two different carbon allotropes – diamond and a-C. These hybrid carbon aggregates likely have bulk properties different to pure diamond as grain boundary energy, mobility, diffusivity, cohesive strength and sliding resistance – all of which determine bulk materials behaviour and properties (Cantwell et al., 2014) – are expected to alter due to the presence of the a-C films.

Conclusions

Commonly used pressure/temperature models for the phase transformations of elemental carbon reflect stability fields for diamond, graphite, liquid and vapour, and diamond and mantle chemistry studies typically focus on what they consider the most relevant of these – the graphite-diamond transition. However, the discovery of a-C in diamond aggregates indicates that the standard carbon bulk phase diagram does not adequately reflect the intricacies of natural diamond transitions and would benefit from updating to include complexion phases.

Acknowledgements

References

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