

A MODEL OF THE FULLERENE CO-CATALYST EFFECT ON THE DIAMOND GROWTH FROM GRAPHITE

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We have recently shown [1] that the graphite - diamond conversion efficiency increases 1.4 times at $P=4.5$ GPa and $T=1200^{\circ}\text{C}$ if 0.015 to 0.3 % fullerene (of the graphite mass) is added to a mixture of a catalytic metal and graphite.

Here we report a model of this effect. It is assumed that cycloaddition of fullerene molecules to graphite sheet edges gives rise to adamantine (diamond-like) structures. This, in turn, leads to nucleation of diamond crystals, which further grow via bulk rearrangement of the whole graphite mass due to a local re-hybridization of the sp^2 -graphite lattice to the sp^3 -diamond lattice. Our model provides a qualitative understanding of the experimentally observed increase in the graphite-diamond conversion efficiency on fullerene addition to a mixture of metallic catalyst and graphite.

When heated to a temperature of synthesis under pressure, fullerene becomes localized at the edges of graphene sheets in a cycloaddition reaction to form adamantine-like structures without hydrogen. Such structures become seeds for diamond growth since they are structurally similar to the diamond lattice. Cycloaddition changes two carbon atoms of graphite from the sp^2 -state to the sp^3 -state, thus perturbing a region on a graphene sheet, which may further initiate the whole process. Simultaneously, the pairs of atoms of the fullerene skeleton undergo a similar transformation. An important contribution to this process may be made by the [2+2] cycloaddition well-known for fullerenes, e.g., dimerization or the reaction with dehydrobenzene.

The fullerene attachment to graphite immediately produces some new reaction centers in the form of double bonds, up to five centers instead of one. This is followed by

formation of nanodiamond crystals bound to the fullerene up to a certain moment. The graphite lattice edge is transformed to the sp^3 -hybridized state to become adamantine-like (diamond-like) and then adamantine-like structures involve the rest of the lattice in the transformation. Subsequently the growth of larger nanodiamonds from the graphite bulk begins by involving adamantine-like structures in the cycloaddition reactions. At this stage, fullerene does not any more react with graphite. The diamond surface itself becomes involved in the cycloaddition reactions, and all graphene sheets are transformed due to the cycloaddition reactions with the diamond.

As the diamond crystal grows, the energy of the "virtual" double bond on its surface decreases because the larger is the crystal, the smaller is the strength of the surface double bonds and the lower its reactivity. The temperature conditions become too unacceptable for cycloadducts, which stimulates the reverse reaction of decomposition to release nanodiamond and fullerene, probably, in a modified state.

From this point of view, fullerenes have two essential advantages over other dienophyls – they are stable up to high temperatures and consist only of carbon atoms. These advantages allow fullerenes to become incorporated, if necessary, into a polymeric carbon structure.

References

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