Revealing the nano-world to understand an age-old process

Dr Heinrich Badenhorst

The University of Pretoria is a world leader in ultra high-resolution scanning electron microscopy. Students in the South African Research Chairs Initiative (SARChI) Chair in Carbon Materials and Technology are using this cutting-edge equipment to peer deep into the structure of carbon materials. They are revealing new aspects of what was thought to be a well-understood and mature subject: the combustion of graphite. By linking their observations of tiny particles and minute structures to innovative models, entirely novel descriptions of the material's behaviour are being created. This work promises to lay the foundation for a much broader understanding of exactly how carbon burns.

Ever since the Palaeolithic cavemen ignited those first flames of fire almost 800 000 years ago, man has striven to harness its amazing power. Combustion is the impetus behind nearly every aspect of our lives – from the cars we drive and the electricity we use in our homes, to the traditional braaivleis that makes our weekends so special.

Despite all the research that has gone into understanding this relatively simple reaction between carbon and oxygen, much is still disputed. This is partially due to the myriad of complex carbon structures that exist. The problem is further complicated by impurities in the material, which can both inhibit and amplify the reaction. A first look at the carbon surface already reveals numerous phenomena. Graphite was chosen as a simplified carbon structure for the initial modelling in this research.

As can be seen in Figure 1, the planes of hexagonally bonded carbon atoms give graphite a characteristic layered structure. This layered structure, along with several other aspects, is revealed in the image. The figure shows that the edges of the graphite are lightly dusted with tiny white particles. These particles inhibit combustion, leading to the development of characteristic edge features. One can also see large droplets of catalyst particles. These catalysts drive the combustion in a multitude of ways, but over time they agglomerate into larger particles and become relatively inactive.

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Initially it was thought that all graphite materials were similar, but closer investigation revealed large differences between natural and synthetic materials. For example, the synthetic materials were found to be far from ideal and much more liable to attack by oxygen, leading to some very complex structures, as illustrated in Figure 2.

Only natural graphite exhibited the pristine edges (Figure 3) with the characteristic 120º angles that are indicative of the underlying crystal structure. In addition, the natural material was found to contain inclusions of impurities. When these were evaporated under extremely high temperatures, the beautiful, underlying layered structures of the flawless graphite crystals were revealed.

Close inspection of the graphite particles showed several noteworthy microstructures. As the particle is combusted, these structures develop and grow, controlling the rate at which the material burns. Based on this observation, several representative structures for the behaviour were proposed and simulated using a probability-based finite element mesh. This allowed the progression of the microstructure throughout the reaction to be predicted, as shown in Figure 4, which could ultimately be linked to real experimental data.

When the edges of the partially combusted natural graphite flakes are examined, the effect of the catalytic impurities are clearly noticeable. The edges are completely degraded and highly erratic as the catalyst particles have created random channels in the graphite. In some cases, the catalyst particles cut fissures into the graphite, which created tiny fjords (each less than one tenth the width of a human hair), as can be seen in Figure 5.

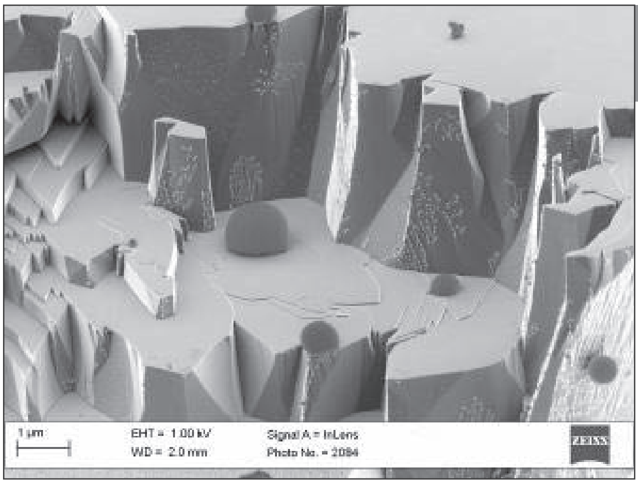


Figure 1: Surface effects on graphite.
(Winner: Carl Zeiss Nano-image Competition)

Figure 2: Synthetic graphite structures.

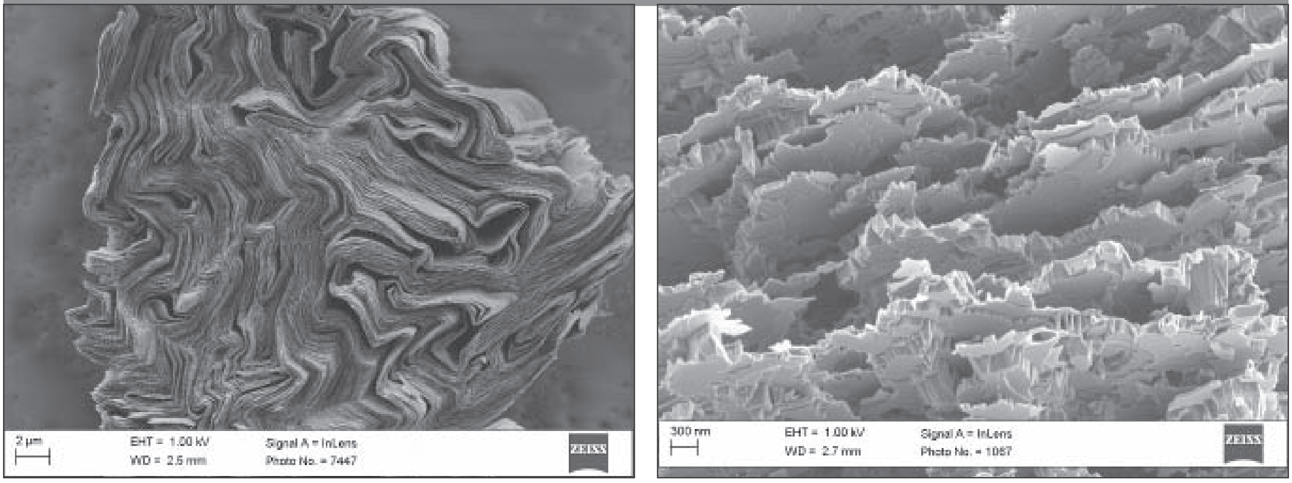
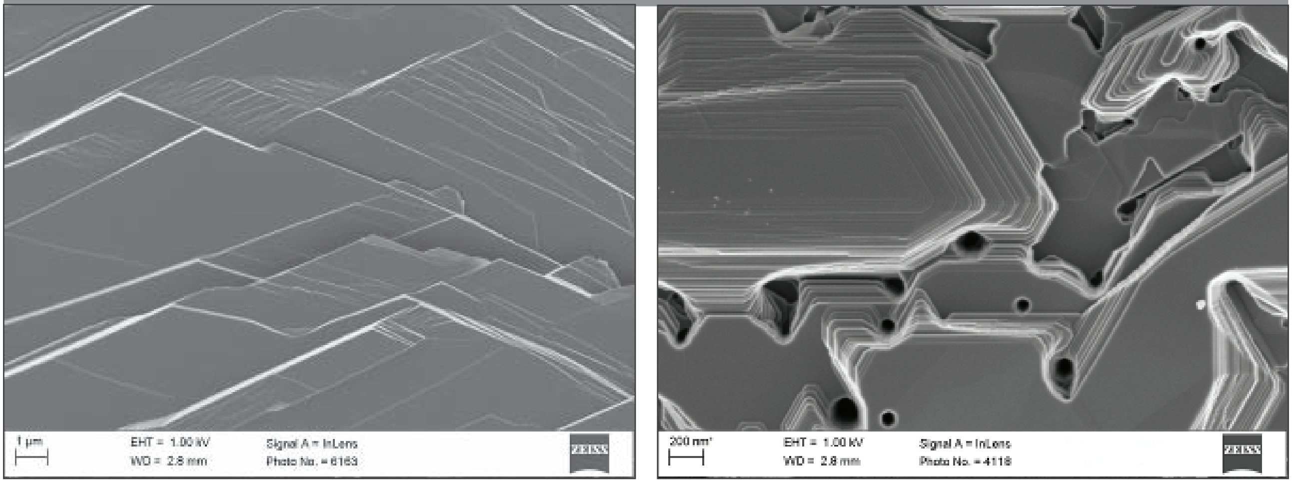
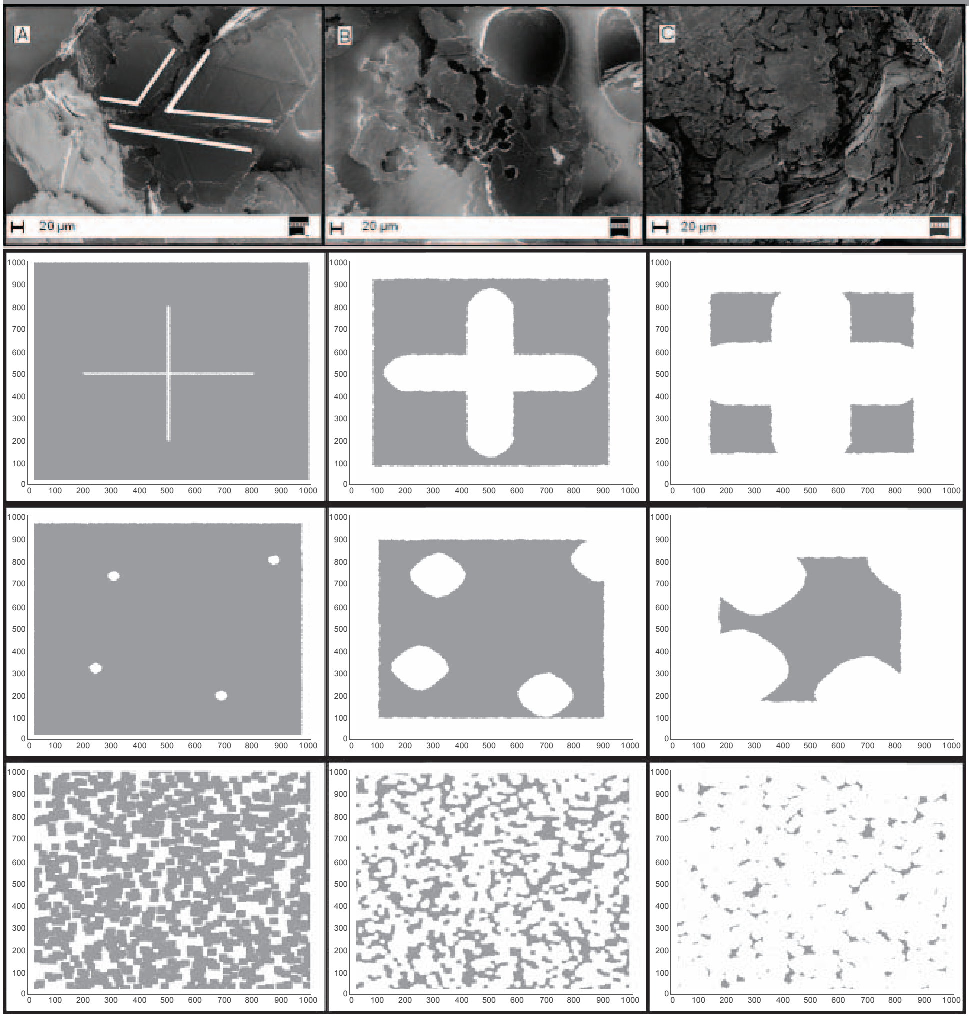


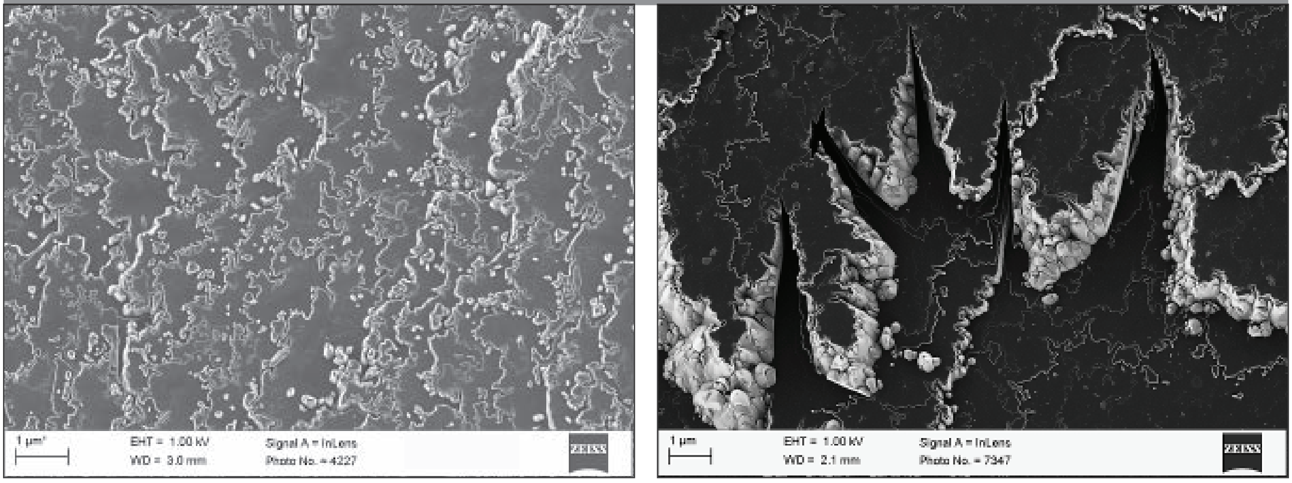
Figure 3: Natural graphite structures.



→ *Figure 4: Microstructural development.*



→ *Figure 5: Catalytic effects. (Winner: NRF Science Lens, Nanotechnology category)*



The particles that cause these effects are extremely small. In most cases they are in the order of a few hundred nanometres, which is about the same size as an average virus particle.

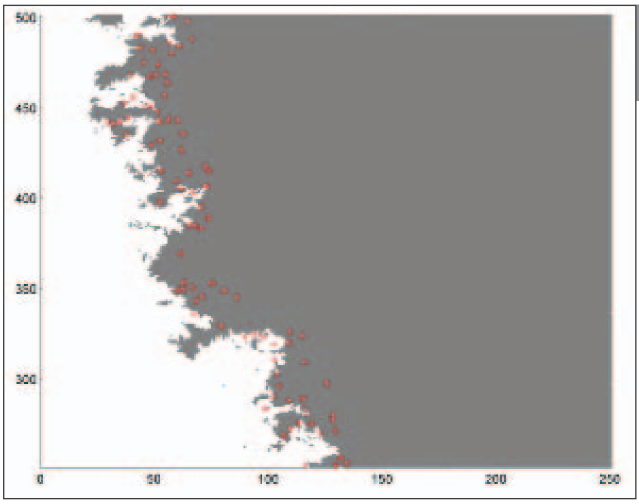
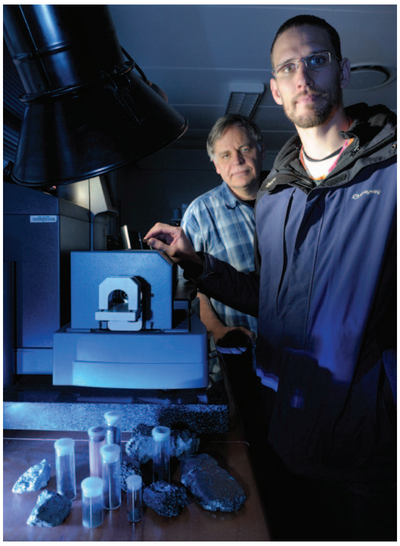


Figure 6: Simulated catalytic particles.

The particles that cause these effects are extremely small. In most cases they are in the order of a few hundred nanometres, which is about the same size as an average virus particle. By studying the wide variety of behaviours these particles exhibit, a general representation of the catalytic action can be formulated. This was incorporated into the aforementioned simulations to account for the effect of the catalysts on the measured reaction rates (Figure 6). The red dots represent individual catalyst particles that trace random channels through the graphite.

Finally, the influence of the particles that inhibit combustion had to be considered. These particles block the attack of oxygen, shielding subsequent layers from attack. This leads to the formation of distinctive saw-tooth-like edge structures, as can be seen in Figure 7. The pinnacle of each structure represents a single inhibiting particle, protecting the entire formation. In some cases this leads to the creation of tiny caves. Within them, minuscule stalactites and stalagmites are visible. It is incredible to imagine that these formations are one thousand times smaller than a single strand of human hair.

All of these phenomena could not have been observed without the exceptional resolution of the modern electron microscope facilities at the University of Pretoria. By incorporating all three of these effects into a single model framework, a coherent foundation has been formulated to study the combustion of a variety of carbon materials. It is hoped to expand this work in the future to include a far wider range of carbon allotropes and impurity behaviours. This work has already borne fruit in the form of several industrial applications aimed at modifying the combustion behaviour of carbon materials. If successful, the new materials will open doors to a wide range of new high-temperature applications for carbon materials.



Dr Heinrich Badenhorst (front) *recently completed his PhD in Chemical Engineering and will soon be taking up a research fellowship at the University of Pretoria. His interests centre around all forms of carbon materials, with a particular focus on surface, structural and kinetic phenomena.*

Figure 7: Inhibitor effects. (Winner: NRF Science Lens, International Year of Chemistry category)