Pyrolytic carbon layers: deposition parameters, grain boundaries, carbon modifications
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Pyrolytic carbon layers have a broad array of industrial applications. Being able to specifically adjust their physical properties is most important, and researchers of the University of Karlsruhe are investigating possible connections between production conditions, microstructure and physical properties. They use light and electron microscopes to do so. Olympus image analysis software is used for microscope control as well as for digital acquisition, management, archiving and evaluation of images and spectra.

Making fine-tuned adjustments

Pyrolytic carbon, known as „pyrocarbon“ for short, is a graphite-like material that can be produced via pyrolysis of a hydrocarbon gas. Pyrolysis is based on thermal decomposition at high temperature and oxygen-free conditions. The pyrocarbon layers that are deposited during this process on adequate substrates are used in a multiplicity of ways by industry: eg, production of brake pads, nozzles and exhausts, solid fuel rockets and anti-oxidant coatings for silicon wafers. Each application area requires coatings with very specific physical, chemical and mechanical properties. These can be adjusted specifically by answering the following series of questions: How are these properties affected by the layers’ microstructure? How is the microstructure dependent upon the chemical elementary reactions taking place during deposition? And how do these elementary reactions depend on the deposition parameters selected?

Microscopy and image analysis

Application-oriented fundamental research done at the University of Karlsruhe aims to explain these dependencies and interrelationships through quantitative and morphological analyses. Light and electron microscopes are used with digital image processing. The Olympus image analysis platforms analySIS and iTEM offer all the necessary functions for microscope control, digital acquisition, management, evaluation and centralized archiving of images and spectra.

Pyrolytic carbon layer under the light microscope (left). The layer morphology can be quantified via area percentages of grains and grain boundaries respectively (s. arrows – left). Digital image analysis makes it easy to determine the respective area percentages (right).
Grains and grain boundaries

Light microscopes are well suited for investigating the grain structure of pyrocarbon layers. The grain structure can be quantified by determining the percentage area taken up by the grain interior and the grain boundaries respectively (fig. 1). The determination of this area percentage is done via digital image analysis. The camera attached to the microscope acquires the image digitally and transfers it to the analySIS image buffer. It is important to have the grains and the grain boundaries reproduced using different gray values. The „Separator“ filter function can differentiate them easily and automatically detects grains and grain boundaries. Particle analysis of the grains is determined according to size and shape; however, in this case the specific grain boundary density is most important.

For technical applications, being able to specifically adjust the physical properties of pyrolytic carbon is important. These properties are primarily determined by the microstructure, and this depends upon production conditions. When pyrocarbon layers are produced via thermal decomposition (pyrolysis) of methane, the methane pressure is one decisive factor that grain boundary density is dependent upon. Digital image analysis made it possible to clarify the exact composition.

Automated extraction

The specific grain boundary density – ie, the percentage area of the grain boundaries – can be obtained as follows: the settings for the „Separator“ are set so as to visualize the grain boundaries. These are then extracted automatically (fig. 1). Phase analysis determines the percentage area of the extracted grain boundaries. Pyrocarbon can be produced from methane, for example. Figure 2 shows several measurement results graphically. The curve shows the correlation between methane pressure and specific grain boundary density. It is easy to see how the microstructure of the pyrocarbon layer changes depending on the respective methane pressure. At a pressure of about 37.5 kPa, a layer of minimum grain boundary density is formed. There is a correlation between this minimum grain boundary density and a maximum degree of layer crystallization. This is one example of how digital image analysis can help clarify and optimize deposition parameters.

Spectral steps forward

An energy-filtering transmission electron microscope (EFTEM) along with the software makes it possible to go
one step further into the microstructure. The goal is to uncover any correlation between the microstructure of the layer and the various types of carbon bonds. If that can be done, it would be possible to draw conclusions regarding the state of the atomic bonds (based on the information provided by the microscope images). Using the EFTEM, high resolution image acquisitions can be combined with analytical spectroscopy investigation. And the EFTEM does not just acquire images. Thanks to the built-in energy filter and the software, Electron Energy Loss Spectra (EELS) can also be acquired. The image analysis software controls the electron microscope to acquire and calibrate images and EELS spectra. The electron beam is aimed at a selected sample position. The digital camera serves as a detector and records how many electrons lose how much energy when passing through that position of the sample. The curves shown on this EELS spectrum are characteristic to the various types of bonds. The curves show which bond type predominates at the spot investigated.

The π peak at 6 eV and the π+σ peak at 26 eV are typical for the graphite spectrum. Diamond does not have a π peak. Amorphous carbon does not have a π peak and has a π+σ peak shifted to 22 eV. The EELS spectra confirm that a graphite-type structure predominates in the pyrocarbon. When compared exactly, however, it is evident that the π peak is weaker along grain boundaries than within the grain interior (fig. 4). Furthermore, the π+σ peak has shifted more significantly to lower energies (see dotted black line). This indicates that along the grain boundaries, the degree of graphitization declines.

Working the digital way

When clarifying interrelationships between production conditions, the microstructure, and the physical properties of pyrocarbon, doing things ‘digitally’ helps a great deal. Being able to acquire light-microscope images digitally, analyzing them interactively and in an automated fashion and archiving them in a well-structured way makes image evaluation and management much easier. It’s also a big help being able to use the same software environment for the electron-microscope investigation. The images and spectra are acquired, the microscope is controlled, and results are displayed graphically – all via the software. All images, spectra, data and results are placed into a central database and are available for later investigation at any time.

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Graphite, diamond and amorphous carbon

Figures 3 and 4 show the result of an EELS investigation of a pyrocarbon layer. The EELS spectrum of grain interiors is shown in bluish violet, the grain boundaries appear dark green. The acquisition length was 5 ms respectively. The spectra used for reference were graphite (blue), diamond (light green) and amorphous carbon, and polymer film (red).