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MORPHOLOGICAL INVESTIGATIONS ON CARBON-BLACK PARTICLES BY ATOMIC FORCE MICROSCOPY

W. NIEDERMEIER, J. STIERSTORFER, S. KREITMEIER, O. METZ* AND D. GÖRITZ

DEPARTMENT OF APPLIED PHYSICS, *DEPARTMENT OF PHYSICAL CHEMISTRY. UNIVERSITY OF REGENSBURG, D-93040 REGENSBURG, GERMANY

ABSTRACT

The atomic force microscope (AFM) can profile surfaces similar to the scanning tunneling microscope (STM) at resolutions down to the atomic level. To investigate carbon-black particles and subsequently styrene–butadiene-rubber, filled with carbon black, a STM was modified to run as an AFM. An optical detection system is used to measure the deflection of the cantilever. Atomic resolution was achieved by forces in the order of $5 \cdot 10^{-8}$ N on mica with the AFM.

Structural investigations of carbon-black particles of different dimensions with the AFM agree with the data of the manufacturer. The model of the microstructure of such particles, built up of 1–3 nm large, tilted domains of graphite structures, could be confirmed. This surface roughness is probably an important parameter for the strengthening mechanism of carbon black in elastomers.

INTRODUCTION

Carbon black is economically the most important active filler for technical products made from natural rubber. Its wide range of applications is a very interesting topic in material science. The filler–rubber interactions are both physical and chemical, ranging from weak Van-der-Waals forces to strong covalent linkages. The portion of each kind is still unknown.[1,2] A reinforced elastomer consists primarily of polymer and filler; and in order to combine these materials effectively, their individual characteristics must defined first. Carbon-black fillers interact with their surroundings by means of their surfaces, which are very large due to the small size of the carbon-black particle.[3] Therefore it is important to get more information about the surface structure of carbon black.

To reach this aim an AFM was built up. Since the advent of the scanning tunneling microscope (STM) in 1981,[4] this new field of research has made rapid progress. The success of this tool spurred the development of a wide variety of other scanning probe techniques, in particular the atomic force microscope (AFM).[5]

The power of the AFM is its ability to study the surface structure of both conductors and insulators. This instrument can profile surfaces similar to the STM at resolutions down to the atomic level. The idea of the AFM is to bring a sharp tip, located at the end of a microfabricated cantilever, into close proximity with the sample, and to move this fine tip over the sample to map the contours of the surface.

The STM detects the tunneling current between the tip and the sample. In the AFM, forces between tip and surface are detected by measuring the deflection of a flexible cantilever. The total force, acting on the cantilever, caused by the tip–sample interaction may be regarded as due to two independent parts.[6] One is the short-range (less than a few angstrom) repulsive force, resulting from charge overlap between tip and sample: this force is localized, and involves only a few of the nearest atoms of the sample. The other part is the long-range (up to hundreds of angstroms) attractive force, called the Van-der-Waals force, resulting from induced dipole–dipole interactions: this force is nonlocalized, and is due to many thousands of the nearest sample atoms.

In order to achieve a high resolution with the AFM a repulsive force is necessary. Only the repulsive force is able to distinguish two points on a surface separated by atomic distances; in contrast the attractive force is only able to resolve structures of the order of the tip radius r.[7]

* Department of Physical Chemistry. University of Regensburg, 93040 Regensburg, Germany.

Our primary use for this instrument is to study the morphology of carbon-black particles of different dimensions, adsorbed on mica.

EXPERIMENTAL

AFM DESIGN

Our instrument is a variation of an earlier STM[8] and can be used as an AFM or a STM. The design of our atomic force microscope is sketched in Figure 1. The center of our instrument is a stainless steel block (14.5 × 6 × 5 cm) with a slit of 1 cm. Two invar manufactured differential screws are used for the mechanical approach.

The sample is mounted on a single tube piezo scanner. The scanner itself is fixed to the differential screw 1. Differential screw 1 provides the rough approach (50 μm per turn) towards the tip. The fine approach is obtained by the second differential screw (DS 2), which is positioned at the end of the steel block. So the small lift is reduced again by the decreasing spread along the slit. This way the gap can be mechanically controlled within very high accuracy (better than 5 nm). This accuracy is sufficient to bring the sample close enough to the cantilever to allow the piezoelectric transducer[9] to accomplish the final approach.

To detect the vertical motion of the tip, which is proportional to the force the tip applies to the surface of the sample, we use an optical deflection system. A light beam of a laser diode is focused on the backside of the lever. A two segment photodiode detects the deflection of the cantilever by sensing the position of the reflected beam. With this setup cantilever displacements of less than 0.1 nm are measureable.

Due to the geometric arrangement, the limiting factor of the vertical resolution is not the sensitivity of the photodiode but rather the sound and building vibrations. The effective noise level is approximately 0.04 nm root-mean-square in the frequency range from 10 Hz to 1 kHz.

METHODS AND MATERIAL

All reported measurements have been performed with repulsive forces in the range of $5 \cdot 10^{-9}$ to $5 \cdot 10^{-8}$ N. The topography of the surface was mapped in the constant-force mode; feedback electronic was used to keep the deflection and thus the applied force constant. For

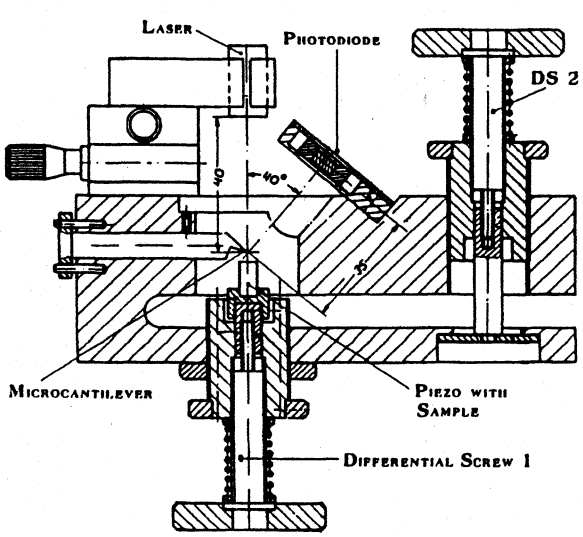

FIG. 1.—Schematic view of the AFM, used in this study.

the experiments we used Si_3N_4 cantilevers with a typical lever force constant of 0.06 N/m, a tip with a radius of curvature less than 40 nm and a length of 200 μm.[10]

The carbon black samples were dispersed in toluene and then placed in an ultrasonic bath to scatter the carbon black agglomerates into aggregates. Afterwards a droplet (about 0.03 mL) of this dispersion was placed upon a freshly cleaved mica surface and dried for 2 days. We used mica as substratum because of its atomic flat surface. This way we avoided superposition of two topographical surfaces. This simple preparation method is a great advantage of the AFM in comparison to transmission electron microscope (TEM) or scanning electron microscope (SEM) investigations. Additionally, the use of an AFM allows three-dimensional pictures of a sample mounted on any substratum.

RESULTS

The performance of the AFM was checked on mica. Mica, a layered insulator, has a surface consisting of SiO_4 tetrahedra which cleaves along flat planes of atoms that can be revealed by the AFM (Figure 2). The nearly hexagonal array of dark spots in the image corresponds to depressions in the center of hexagonal rings of SiO_4 in these planes. This well defined hole-to-hole distance of 0.52 nm[11] could be used to calibrate the instrument. Figure 2 proves that the lateral resolution can be better than 0.3 nm. This demonstrates that the AFM is a powerful method for studying surface roughness with high resolution.

Table I gives an overview of the investigated carbon blacks, manufactured by furnace technique.[12] The first column specifies the average diameter of primary particles; the second column gives the specific surface. The effects of these parameters are as follow: with increasing specific surface the activity and the strengthening mechanism of carbon black increases. The smaller the average diameter of primary particles, the greater the strengthening mechanism.

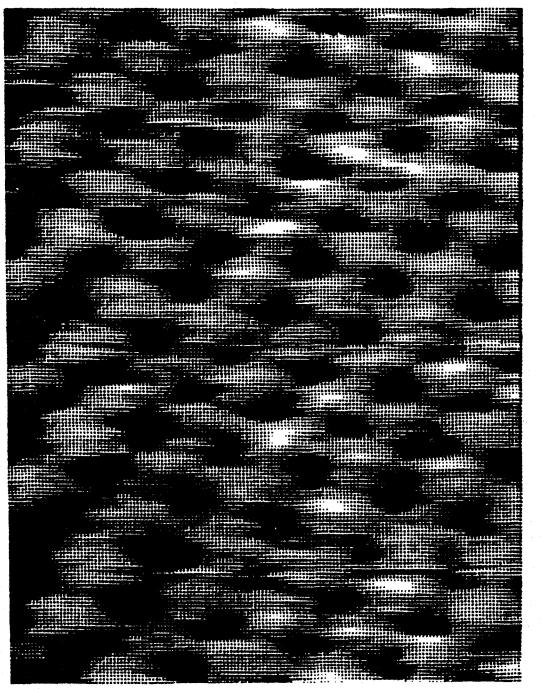

FIG. 2. — Unfiltered image of atomic corrugation on mica in air. The period of the hexagonal pattern is approximately 0.5 nm; image area is 5.0 × 3.8 nm^2.

TABLE I

CHARACTERISTIC DESCRIPTION OF THE MANUFACTURER[12]: ARITHMETIC AVERAGE OF THE PARTICLE DIAMETER AND SPECIFIC SURFACE

Carbon black	Average diameter [nm]	Specific surface $\left[\frac{m^2}{g}\right]$
N990	300	10
N762	70	29
N110	20	140

CARBON BLACK N990

The N990 carbon black is essentially different from all other sorts of carbon black. The primary particle diameter of 300 nm is very large in comparison to the other ones. In Figure 3 it can be clearly seen that the single particles are linked to chainlike structures. This effect is caused by the attractive Van-der-Waals forces. In spite of the large scan area, 2450 × 2450 nm², the image shows individual particles. The average height of the aggregates can be estimated to be 250 nm and the lateral extension to be 300 nm.

CARBON BLACK N762

Figure 4 shows a typical 930 × 930 nm² scan on N762. In the vicinity of the arrow you can see that the carbon black agglomerate is composed of single particles. The particles with

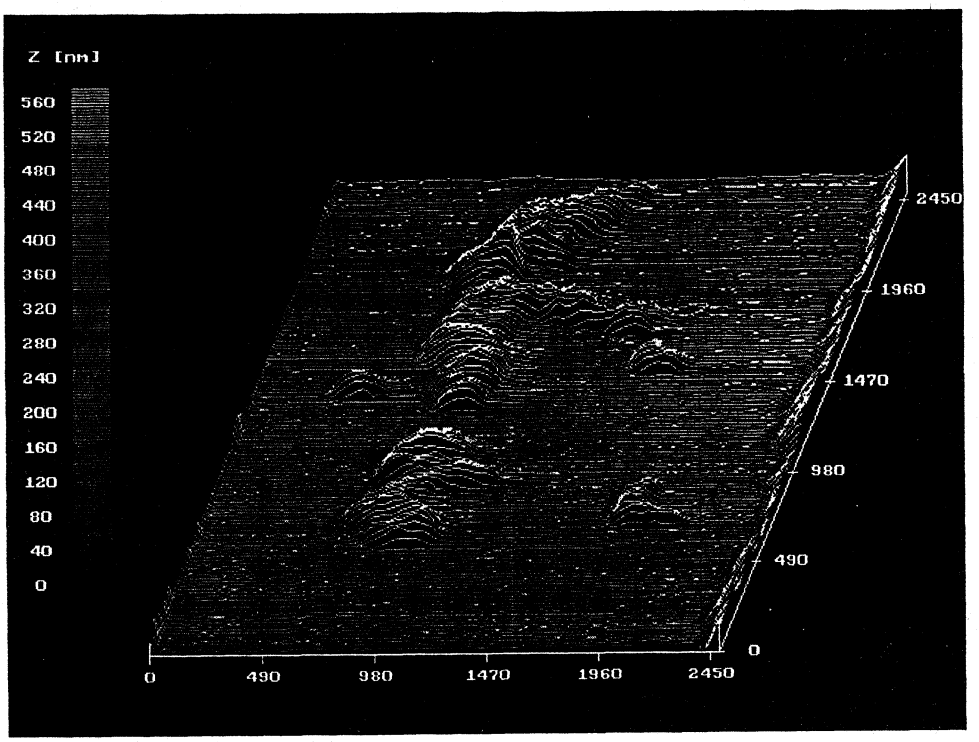

FIG. 3. — AFM image of surface topography of N990 carbon black on mica. The primary particles accumulate to agglomerates and form ramified structures. The diameter of the particles is 250–300 nm; grey scale spectrum covers 560 nm; scan area is 2450 × 2450 nm² (the axes are subdivided in five sections).

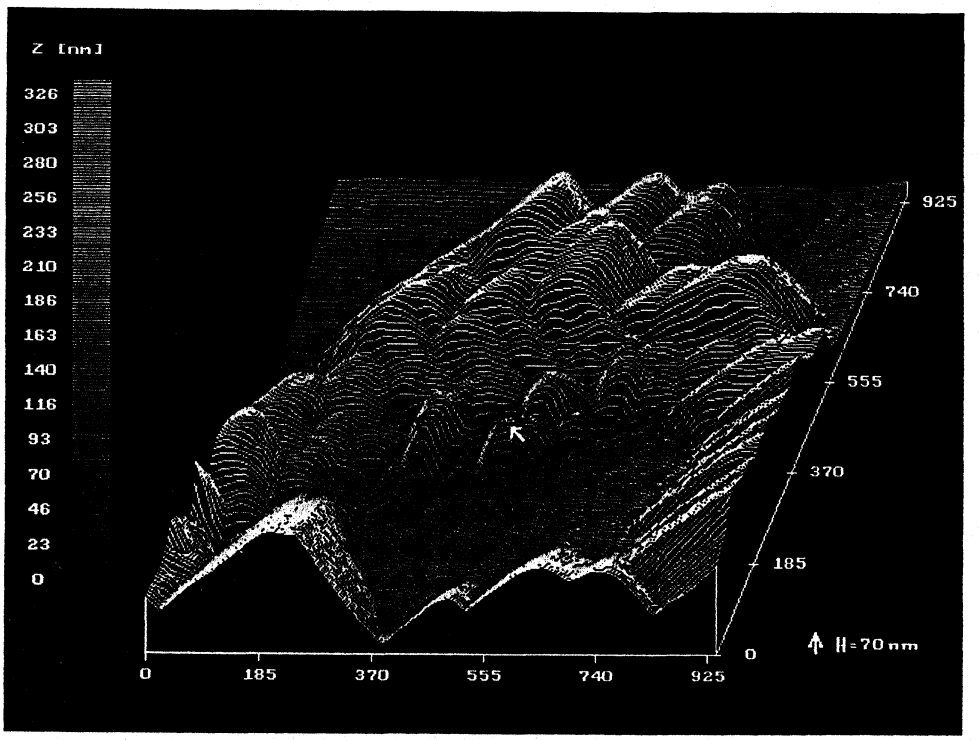

FIG. 4. — AFM image of typical surface topography of N762 carbon-black on mica. The primary particles can be observed (white arrow) with diameters of 65–75 nm. The grey scale spectrum covers 326 nm; scan area is 925 × 925 nm².

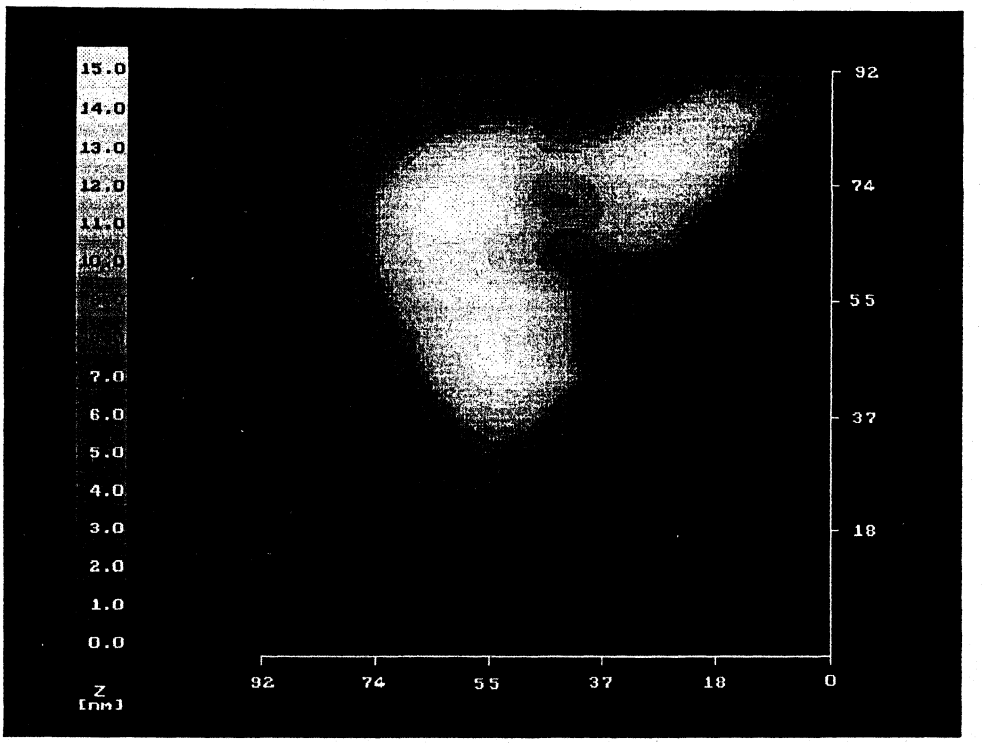

FIG. 5. — AFM image (top view) of 4 single carbon-black particles (N110) with diameters of 16–20 nm. On the left side there are 3 agglomerated particles. The grey scale spectrum covers 15 nm; scan area is 92 × 92 nm².

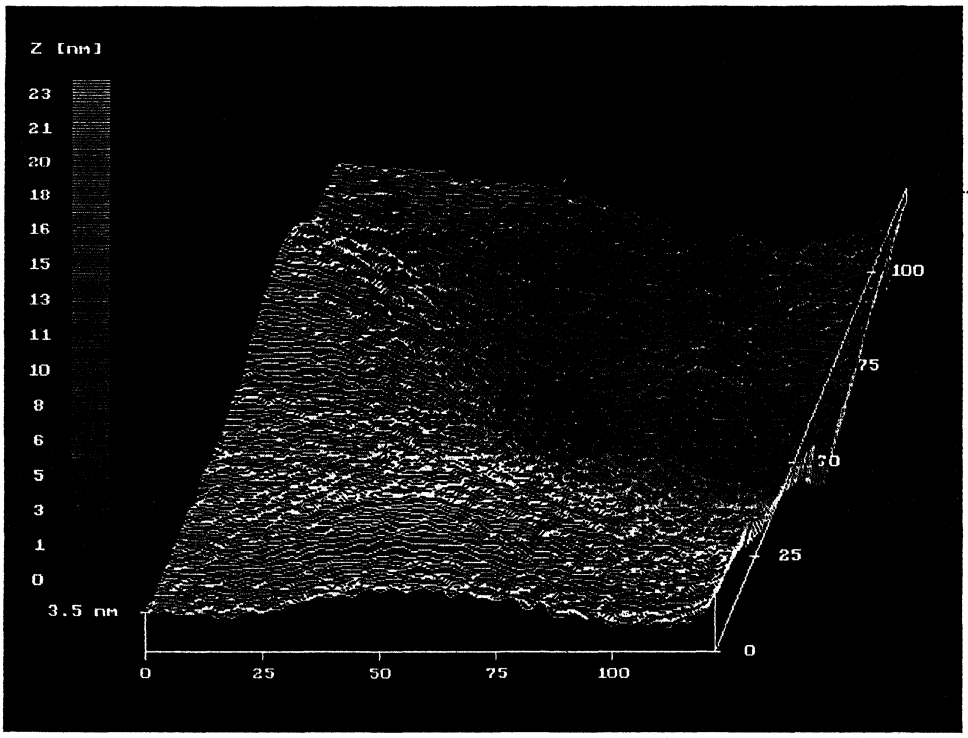

FIG. 6. — AFM image of surface topography of two N762 carbon-black particles showing the idea of tilted domains. The grey scale spectrum covers 23 nm; reference height is 3.5 nm (left bottom corner); scan area is 123 × 123 nm².

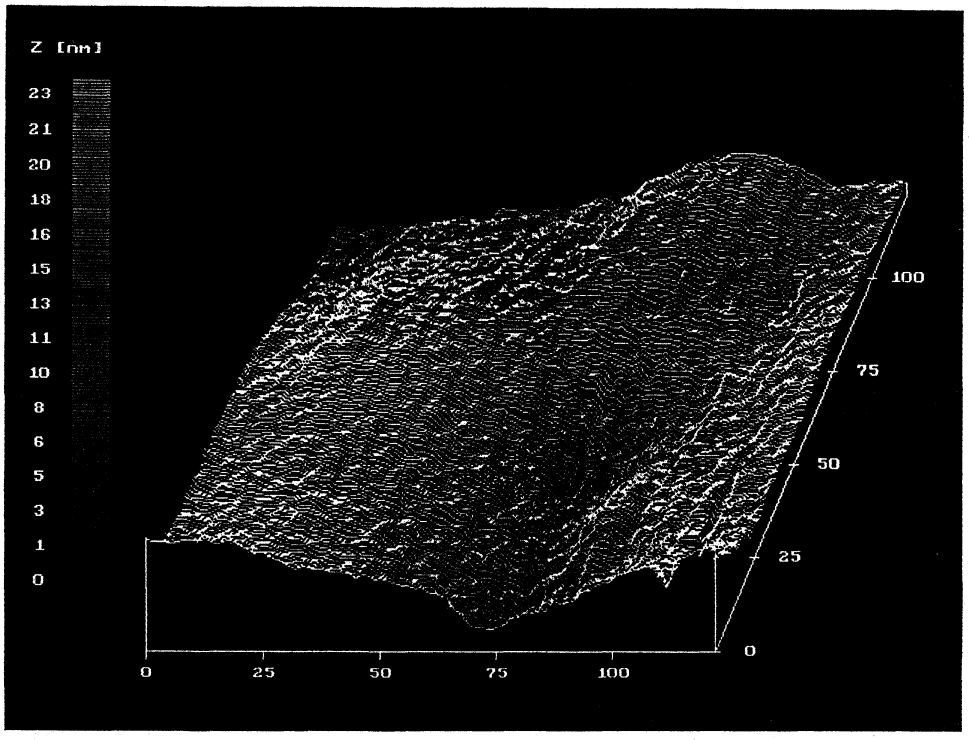

FIG. 7. — AFM image of surface topography to N762 carbon-black particles shown in Figure 6 after rotation by 90°. No vibrations of the cantilever can be observed.

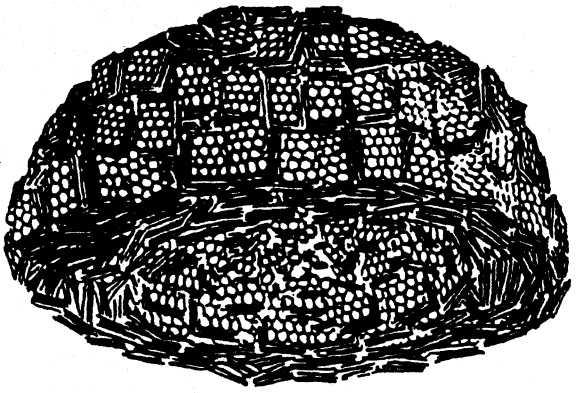

FIG. 8. — Model of the microstructure of a single carbon-black particle.[16] The perspective drawing shows the arrangement of the crystallites. The layer planes are tangential to the particle surface.

their smaller diameter of 65–75 nm build up a structure which differs by far from the one seen with N990.

Obviously the attractive force between the particles is bigger and therefore they build larger agglomerates. The particles pile up and form three dimensional structures. This different behavior is thought to be due to a different surface structure which implies higher attractive forces.

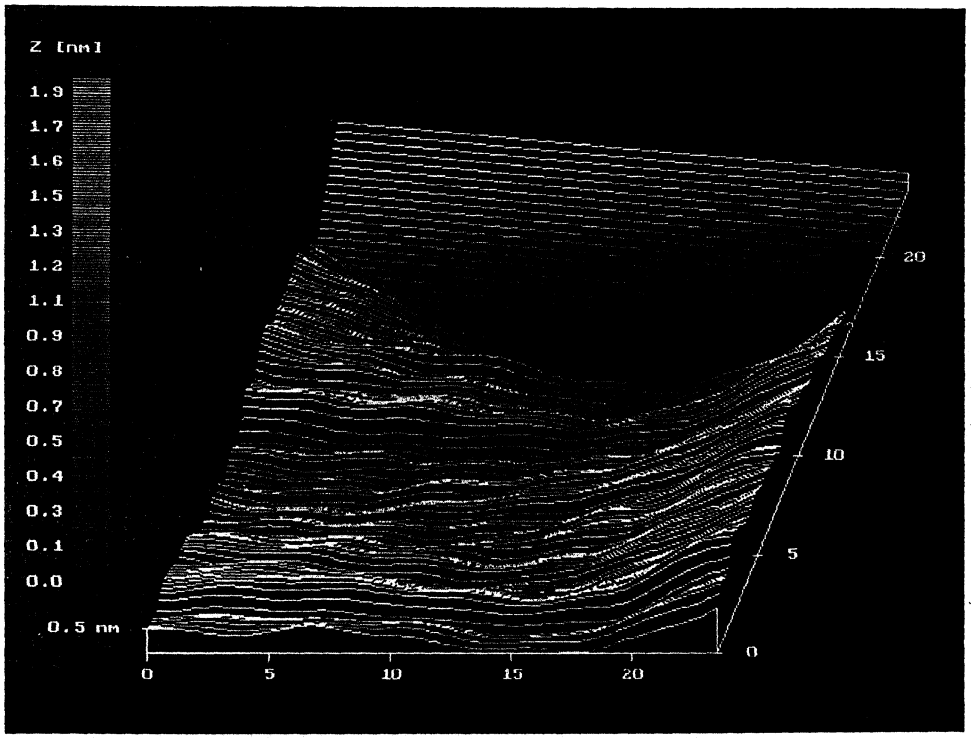

FIG. 9. — High resolution AFM image of the surface of a N762 particle. You can see clearly the tilted domains of about 2 nm extension in the lateral and about 0.2 nm extension in vertical direction. The grey scale spectrum covers 1.9 nm; reference height is 0.5 nm; scan area is 24×24 nm^2.

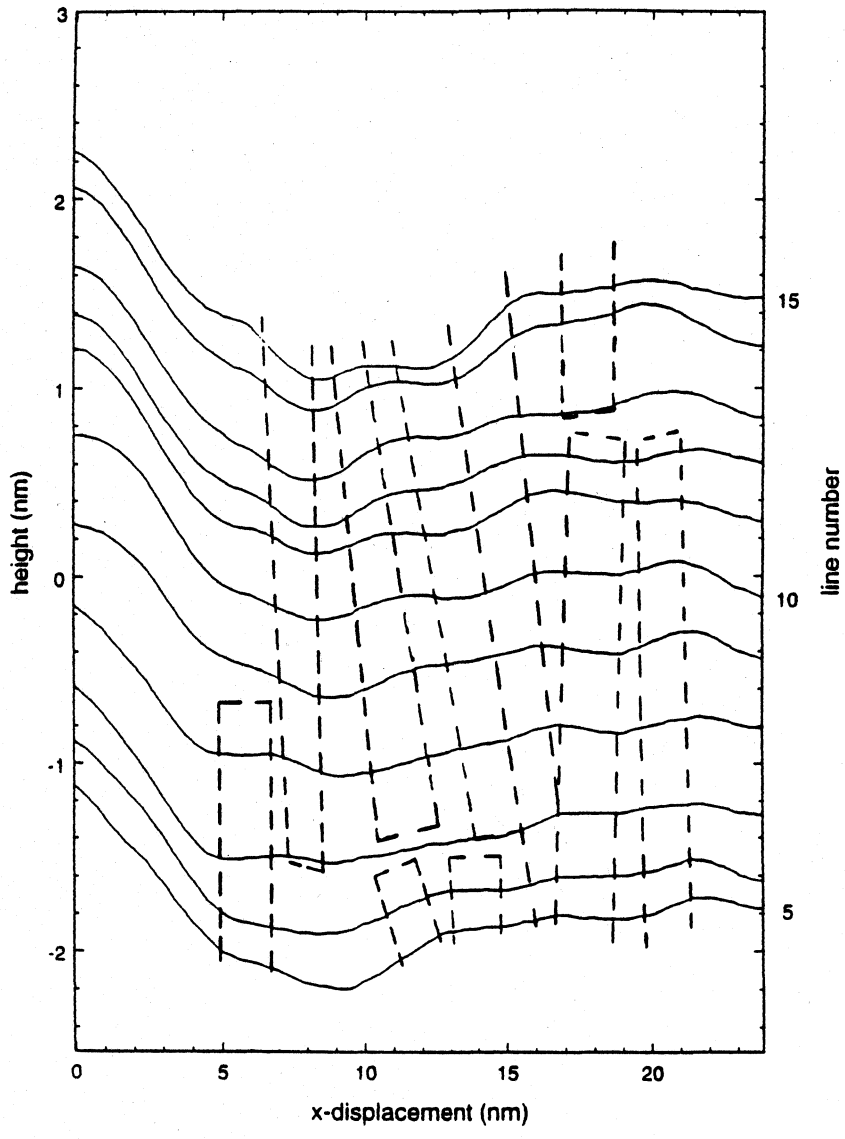

FIG. 10. — Eleven scan lines from high resolution AFM image of N762 particle surface shown in Figure 9. The spacing between two scan lines is about 0.2 nm. The dashed lines illustrate the crystallite planes in top plan view to help visualize real surface.

CARBON BLACK N110

The single particle diameter of carbon black N110 is only about 20 nm, therefore the surface activity and the strengthening mechanism is high. This favors the agglomeration of particles. In spite of the small diameter of the single particles, the surface structure of those agglomerates is on a larger scale not homogeneous but very rough.

In the next figure we choose another graphic representation, which is more plastic and gives a top view of the investigated surface. Figure 5 shows a small scan area of 92 × 92 nm^2 on one of those agglomerates. Three particles lying close to each other can be observed. It seems that the particles are agglomerated because between the three bright spots there is only a very small neck in comparison to the single particle lying beside. The width of this

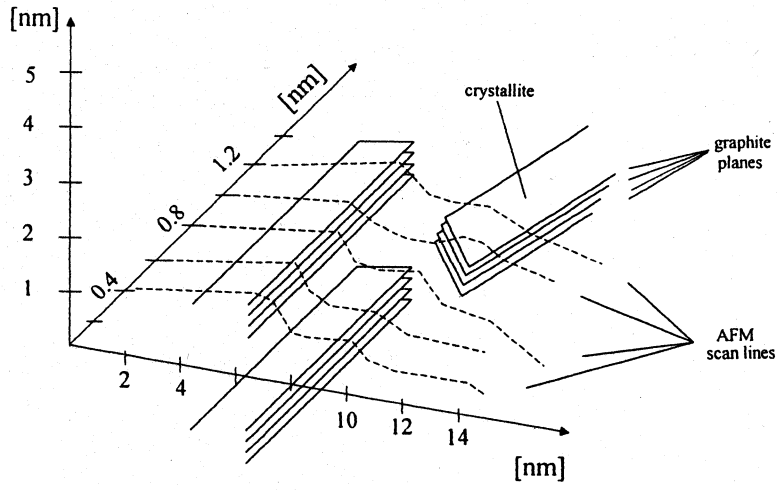

FIG. 11 — The dashed lines symbolize schematic scan lines of AFM on tilted crystals lites. The parallelism of the scan lines changes at crystallite boundaries.

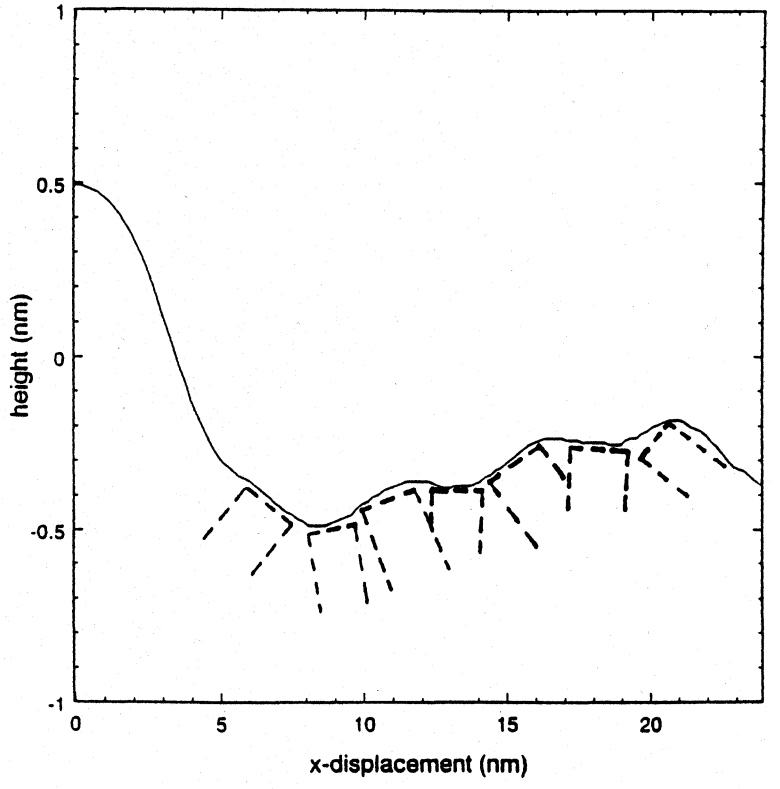

FIG. 12. — Amplitude of the 10th scan line from high resolution AFM image at N762 particle surface shown in Figure 9. The dashed lines illustrate the crystallites in vertical view clearly showing the tilt of the single crystallites. The vertical extensions of the steps are about 0.1–0.3 nm; lateral extensions are about 2 nm.

formation is about 20 nm, corresponding to the average diameter of one particle reported in the literature. Thus the length of a 3 particle formation should be 60 nm, vs. a measurement of approximately 50 nm. This also hints of agglomeration. The diameter of the particles can be estimated to 16–20 nm, which is in good agreement with the literature value.

SURFACE STRUCTURE OF N762

To get more data about the surface structure of carbon blacks we made small scans on two particles of N762. The result of scanning a small area, 123 × 123 nm^2, is displayed in Figure 6. The top of every particle can be recognized by the white spots. Figure 7 is identical to the previous image, only the presentation is rotated by 90°. No effects (respective jumps of the tip) of the scan direction can be recognized in this image. Hence no vibrations of the cantilever are present, demonstrating the high quality of the scan. The observed surface topography of Figures 6 and 7 suggests tilted domains of graphite structures.

Specific preparation methods made it possible to study carbon blacks intensively by X-ray diffraction and transmission electron microscopy (TEM). On this basis many models have been proposed for the surface structure.[13,14,15] A model by Heidenreich[16] illustrating crystallite orientation in carbon black is shown in Figure 8. For the sake of simplicity this is given as a cutaway view of a single spheroidal particle. X-ray diffraction studies have shown that most commercial carbon blacks are made of crystallites which average about four graphite layer planes. The layer planes are roughly parallel and equidistant. The stack height of the crystallites is in the range of 1.1–1.7 nm.[16,3,17] The horizontal extension is about 1.5–2.4 nm. The spacing of the layer planes is in the range 0.35–0.37 nm, being larger than in graphite. The thickness of the layer is 0.28 nm. In the following paragraphs we compare this model to our results.

At a higher level of magnification (Figure 9) the surface forms a step-like structure. This arrangement, which covers all the carbon-black surface, arises from tilted domains of graphite structures. To study the microstructure in more detail, eleven scan lines of the AFM image in Figure 9 are shown graphically in Figure 10. Since the spacing between two scan lines is approximately 0.2 nm, the distance between the first and the last scan line is only 2.2 nm; the x-range is 24 nm. This different scaling is the reason for the elongated shape of the graphite planes shown in Figure 10. It can be used to imagine the lateral arrangement of the crystallites on the real surface. The dashed lines hint the contours of the crystallite planes. The similarity of single sections of adjacent scan lines determines the arrangement of the planes. If this parallel structure disappears from one to an other scan line, a change of crystallites takes place. The sketch gives an idea of the tilt of the crystallites. The lateral extensions could be estimated to be about 1.8–2.4 nm.

Figure 11 shows schematically the scan lines of an AFM made on tilted crystallites of graphite planes. This picture is designed to give a clearer imagination of the measured surface and illustrate our interpretation of Figure 10.

Figure 12 displays the 10th scan line of the high resolution AFM image to point out the tilt of the crystallites and to give an estimation of the vertical dimensions of the tilt. The vertical dimensions are usually in the order of 0.1–0.3 nm, corresponding to the thickness of a graphite plane, but the vertical dimensions range up to 1.5–2 nm, corresponding to the extension of a crystallite.

The comparison with the model by Heidenreich (Figure 8) shows good agreement with the surface structure measured with the AFM. Every single particle is built up of stacks of small parallel-arranged layers of graphite. The dimensions of a layer range from 1.8 to 2.4 nm. The stacks are concentrically grouped in the outer areas of a particle. To form a sphere they must be tilted, building up a step-like structure. This can be seen in our AFM measurements.

CONCLUSION

In this work the AFM was used for a systematic study of surface topography of carbon black. With the AFM the formation of agglomerates can be investigated and the diameter of

single particles can be measured. Detailed images of the N762 surface corroborate a corrugation model for this carbon black. The step-like structure of the surface is clearly evidenced. In contrast to earlier investigations of the specific surface based on gas adsorption, the surface here is directly visible. To our knowledge, this is the first time that clear dimensions could be obtained for unmanipulated tilted graphite structures.[3,18,19]

The surface is increased based on the observed microstructure. Thus, more adhesion sites are available for additional crosslink points between natural rubber and carbon black. The edges of the graphite layers may play a further role. They prevent a slipping of the rubber molecules under extensional force to a larger extent than in the case of a flat surface. Altogether, this leads to a better strengthening behavior of carbon black.

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