DELAMINATION OF GRAPHITE SHEETS IN STIRRED MEDIA MILLS

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Abstract

The structural changes of graphite particles during wet grinding in a stirred media mill have been investigated by scanning electron microscopy, atomic force microscopy and X-ray diffraction analysis. A delamination of the graphite sheets occurs in the shear field of the mill. With an appropriate stabilization method thin graphite flakes with a thickness smaller than 10 nm could be produced.

Introduction

Graphite is a well-known allotropic form of carbon. It consists of stacks of parallel two-dimensional graphene sheets. Each carbon atom is covalently bonded to three neighbors in plane with atoms placed in the corners of hexagon. The graphite structure is characterized by its strongly anisotropic behavior due to the strong covalent forces inside the graphene layers and the weak van der Waals forces perpendicular to the sheets. As a consequence the mechanical, thermal and electrical properties of graphite are highly anisotropic. Graphite and especially graphene are known as promising materials for applications in the field of electronics.

Results and Discussion

In this paper we will present results of different grinding experiments in the stirred media mill. For this purpose the initial graphite particles are dispersed in water and afterwards stressed under different milling conditions (rotational speed of the stirrer, milling bead size). Beside the breakage of the particles between the milling beads, a simultaneous stabilization of the new created surfaces against agglomeration is necessary to advance the grinding progress. Especially in the submicron size range large interparticle interactions and high collision rates of the particles can lead to agglomeration or in the case of a multi-layered material to rearrangement of the single sheets [1]. Therefore different stabilization mechanisms have been investigated. Steric stabilization with polymers as well as electrostatic stabilization with ionic surfactants was used in the milling experiments. By means of X-ray diffraction analysis, SEM and AFM measurements we found that a delamination of the graphite layers occurs in the shear field of the mill [2]. Figure 1 shows a graphite particle before stressing in the mill.

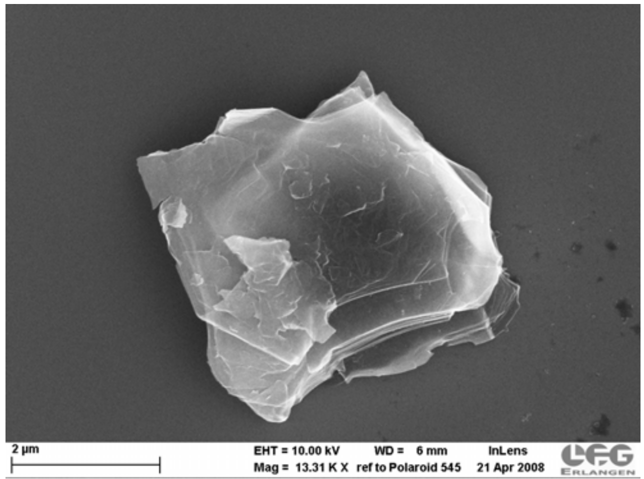

Figure 1: SEM picture of the graphite before milling (feed material)

During the milling process we observe nearly no breakage along the graphene planes, but a good grinding progress perpendicular to the sheets. An optimization of the stabilization mechanism and the milling process, i.e. the use of smaller milling beads, enables the production of extremely thin graphite flakes with a thickness smaller than 10 nm but a mean diameter of about 1 µm. In figure 2 and 3 graphite flakes after different milling times and stabilization methods are shown. One can observe in figure 2 that the graphite sheets are extremely thin and seem to be very flexible. The thickness of the graphite flakes was obtained by AFM measurements. A typical height profile of a very thin graphite sheet is shown in figure 4.

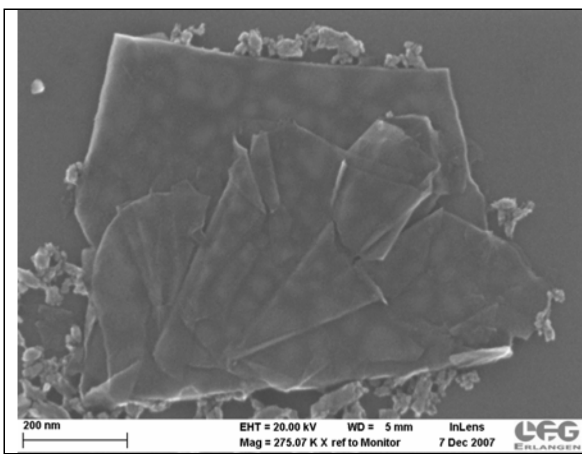

Figure 2: Flexible graphite sheets after 15 h of milling, stabilized with a polymer.

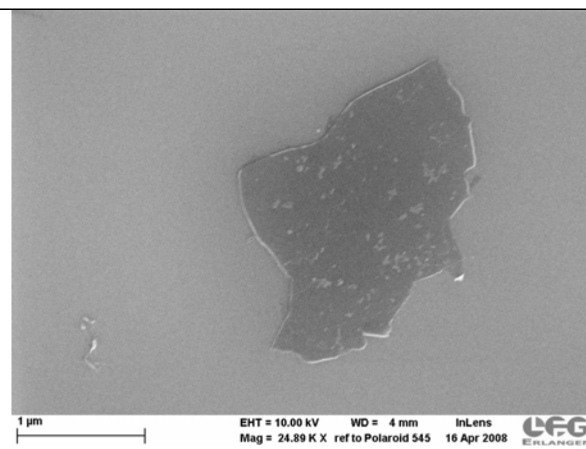

Figure 3: Graphite sheet after 5 h of milling, electrostatically stabilized with ionic surfactants.

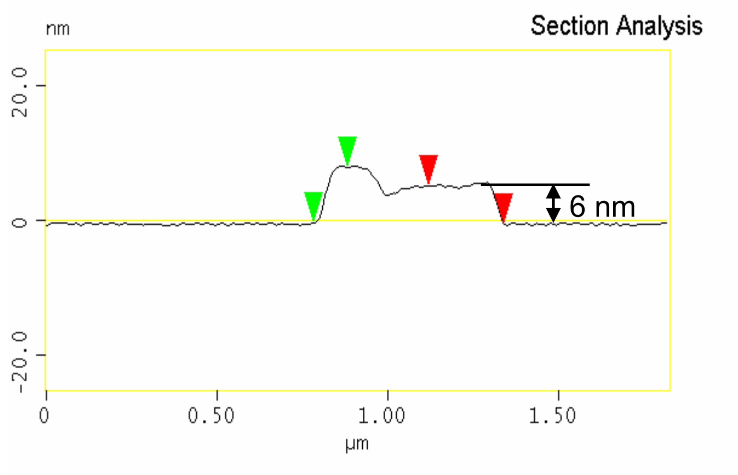

Figure 4: Height-profile of a graphite flake (milled for 5 h, electrostatically stabilized) obtained by AFM measurements.

Under the mild milling conditions with small stress intensities (small milling bead size, low rotational speed of the stirrer) the crystalline microstructure in a layer will barely be affected. Therefore the specific properties, for example the electrical conductivity along a graphene layer, are still present after stressing. In addition we found out that those thin layers seem to be very flexible. This opens totally new applications in the field of printable electronics. In general we showed for graphite particles as an example of a multi-layered material that it is possible to reach a selective and orientation depending comminution which can be controlled by the stabilization mechanism as well as the milling process parameters.

Conclusion

An exfoliation of graphite sheets could be achieved by stressing graphite particles dispersed in water in a stirred media mill. During the grinding process the created graphite-flakes could be stabilized electrostatically as well as sterically to avoid a rearrangement of the exfoliated sheets. Therewith flake like particles with a thickness in the lower nanometer range were produced in the milling process. By changing the stabilization method and the process parameters the morphology of the graphite sheets can be controlled.

References

[1] Stenger, F., Mende, S., Schwedes, J., Peukert, W.; *Nanomilling in stirred media mills*, Chemical Engineering Science (2005), 60(16), 4557-4565

[2] Milev, A., Wilson, M., Kannangara, G. S. K., Tran, N.; *X - ray diffraction line profile analysis of nanocrystalline graphite,* Materials Chemistry and Physics (2008), 111(2-3), 346-350.