RECENT DEVELOPMENTS IN THE PRODUCTION AND INVESTIGATION OF CARBON FIBER REINFORCED COKE

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Introduction

The basic structural element of all graphitic carbon is the graphene layer, which possesses in plane an extraordinary high binding energy (430kJ/mol), providing extreme stiffness and strength. The transfer of these unique properties into a graphitic material would result in revolutional applications. This goal could be partially realized by the development of carbon fibers, which receive much attention as reinforcement for polymers, carbons and ceramics, exhibiting outstanding mechanical properties at low density.

Based on these high performance materials, the idea raised up to combine a polygranular graphite mass product with carbon fibers, enabling a route for traditional graphite products to be resistant under more severe conditions.

Addition of a fiber material into the green mix is a state-of-the-art technique, but the reinforcement is limited to the binder coke matrix. This matrix usually represents just a minor part (<15%) of the raw material mix, which is not necessarily the weakest part of the graphite product regarding fracture mechanics, as observed in crack propagation patterns. Coke grains might be sensitive to cracks, passing through micro-cracks or driven by the lamellar structure of a needle coke.

Going one process step backwards to coke raw material manufacture opens the possibility to introduce a fiber material "in-situ" into the coking device during formation of coke from liquid feedstock. Cracking and condensation should take place in the presence of the fiber, which is offering additional precipitation surface.

In the present study, an overview is given about the technical solution to introduce fibers into the delayed coking device, different fiber morphologies used and their impact on fiber dosing, the coke formation and coke properties. As a result, properties of graphite samples manufactured from different cokes are compared and correlated to graphite samples with fibers in binder matrix only.

Experimental

Experiments were carried out in a technicum scale delayed coker. Atmospheric distillation residue was used as feedstock together with some minor amounts of FCC slurry and a recycle fraction from the coker cracking fraction. The coke yield was around 20-25% and was resulting in 3kg of green coke obtained for each run.

Two experimental options were excluded right from the beginning, because the probability of success was proven to be very low. Chopped fibers dispersed in the feedstock and entering the drum through the bottom led to fiber accumulation in the inlet after initial coke formation and after short time the system would be blocked. Secondly, placing the fibers in the drum before start up of coker, did not lead to the desired product, because upstream of evolving gaseous cracking products is not powerful enough to fluidize chopped fibers in the drum. Coke formation started mainly on top of the fiber layer, while the fibers remained nearly unbounded in a poor coke filled area.

Finally, for the addition of fibers, an autoclave vessel (1l), made from steel and glass was installed on top of the coker drum and connected via a vertical steel pipe to allow fibers a free fall on top of the forming coke bed. Dosing was conducted using a modified rotating shaft in the autoclave, similar to a screw conveyor (Fig. 1a).

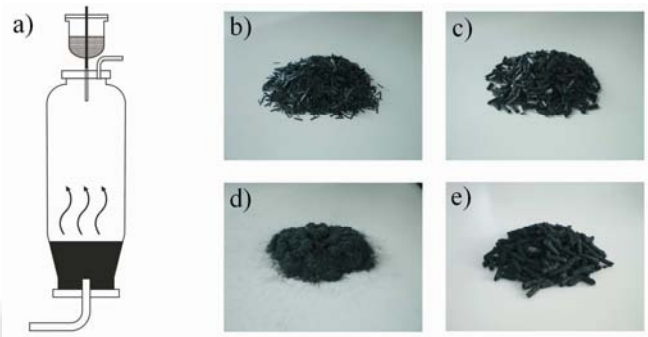

Fig. 1 a) Coker drum / autoclave fiber dosing unit setup, b) PAN based chopped fibers, c) Pitch based chopped fibers, d) milled fibers, e) with epoxy resin pelletized milled fibers

For all experiments, short (or chopped) fibers were considered. The desired amount of fibers was 5-10 wt-% related to amount of green coke. Four different fiber types were tested, including tow types of conventional chopped fibers, milled fibers and chopped composite material from recycled CFRP, which are summarized in Fig. 2b-e. Milled fibers were too fine for direct dosing with existing setup. The fibers were mixed with an epoxy resin (1:1) and extruded through a sieve, cured at elevated temperature and broken into pellets to obtain morphology similar to chopped fiber chips.

The coke was calcined at a temperature of 1200°C and subsequently, milled and screened to prepare a green mix granulometry. Coke was extruded with binder pitch to small rods (ø = 20mm), which were baked and graphitized (Fig. 3b). Specific graphite properties as electrical resistivity, apparent density, coefficient of thermal expansion and mechanical properties were determined. Furthermore samples were investigated using electron microscopy and x-ray techniques.

Results and Discussion

In a delayed coker device, liquid feedstock is preheated to a temperature above the decomposition temperature of organic compounds (>500°C) and consecutively directed under pressure into the coking drum. Relaxation in the drum causes vaporization of feedstock together with the initiation of the delayed decomposition or coking, which gave the process its

name. Heavy decomposition products condense to form a coke matrix while the light compounds evolve though an upper vent for further rectification into different liquid fractions. A coke column is formed, growing up from the bottom and containing small channels, which allow up streaming gases to pass through and condensate on top of the coke column. Coke properties could be tailored for the desired applications, mainly by adjusting coking process conditions, as pressure, temperature, federate and others.

The first challenge for the fiber addition experiment was the design and engineering of a device, which allows the dosing of fibers into the coker drum. Requirements to the device were, to hold the pressure of the drum, transport the fibers continuously into the drum, no necessity for major modifications of the coker system and to guarantee a homogeneous distribution of the fibers in the coke matrix, actually the most important criteria. A dosing system was implemented, which release fibers continuously on top of the solidifying coke column over the whole period of the coker run.

This technical approach was successfully implemented using chopped fiber materials. It was observed, that fibers were evenly distributed over the whole length and diameter of the coke column. The fiber chips were completely entrapped within the coke matrix. After milling of the calcined coke to grains, ready for green processing, a pseudo-needle shape was observed, derived from the morphology of the fiber chips. This led to a preferred orientation of grains during extrusion, a benefit for the production of anisotropic graphite.

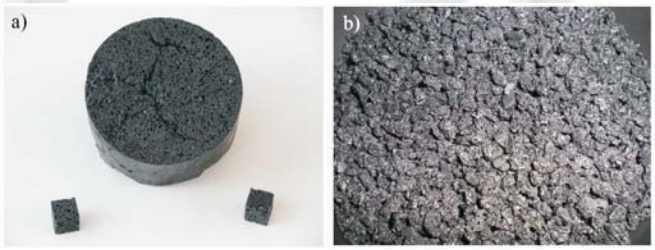

Fig. 2 a) Cutted pieces from green coke column, b) Pseudo-needle shaped coke grains from chopped fibers

In another experiment, fiber bundles were substituted by milled fibers to increase dispersion of fibers in the matrix. For graphite production, usually coke is, at least partially, grinded down to sub-millimeter grain sizes. That means, fiber bundles with a length of several millimeter could only contribute to the reinforcement of very coarse grains. The dosing of milled fiber material was supported by an epoxy resin binder to form small pellets. The resin with a coke yield close to zero released the fibers in the heated drum. The dispersion was, as expected, very high, that fibers could not be detected visually in the coke. Unfortunately, this high dispersion has a minor impact on coke properties compared to fiber chips, when adding equal quantities.

The concept of fiber reinforced coke is also an interesting option for disposal of the increasing quantities of CFRP scrap material which will be provided by the lightweight construction industry in the near future. The material can be shredded to small pieces (Fig. 3a). Disadvantage for the existing dosing unit is the irregular shape of these pieces and probably needs some alternative dosing technique, but effect on coke is expected to be similar as for fiber chips, what is currently under investigation.

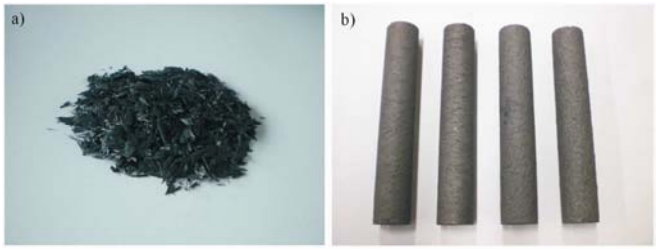

Fig. 3 a) Shredded CFRP, b) extruded graphite rods

The detailed results, which will be presented, show, that specific properties of coke and resulting graphite products, e.g. coefficient of thermal expansion, can be significantly influenced with incorporation of fibers. Differences in mechanical properties are assumed, but can hardly be proven due to the low quantities of coke from each run and the relatively small sample size. A study on the benefit compared to fibers added to the green mix and up scaling consideration will be presented as well.

Conclusions

A suitable technical approach for the addition of fibers into a delayed coker was development and it was proven, the basic concept of carbon fiber reinforcement of coke is working. It was evaluated to some extent, how much impact the fibers have on specific graphite properties. It is pointed out, how to receive a high quality petroleum coke material, which justifies the benefit for graphite properties with additional effort and cost. If these issues could by successfully proven, an upscaling on an industrial coker could be considered within the next few years to obtain an innovative raw material for polygranular carbon and graphite products.

References

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