

PRODUCTION AND STRUCTURE OF EXPANDED GRAPHITE/COKE/ZrC COMPOSITES

Ivan M. Afanasov^a, Gustaaf Van Tendeloo^a
and Andrei T. Matveev^c

^a Chemistry department, Moscow State University,
Moscow, 119991, Russia

^b EMAT, University of Antwerp, Antwerp, B-2020, Belgium

^c Institute for New Carbon Materials and Technologies,
Moscow, 119991, Russia

Introduction

Carbon materials with improved mechanical and thermal properties are appealing subjects for high temperature applications. Among a variety of carbon materials expanded graphite (EG) is a suitable one for the production of high temperature reflecting shields [1] and heaters [2]. For these applications EG should be compacted which is usually performed by uniaxial compression. Alternatively EG may be self-densified through a so called “chemical compression”, i.e. thermal shock of expandable graphite in a tightly sealed container [3].

ZrC is a well-known high temperature material which exhibits both remarkable mechanical strength and chemical stability and hence can be employed for the enhancement of the properties of EG-based compact materials, especially if produced in the form of fibers. The promising method to produce ZrC fibers is a convenient thermolysis of cellulose modified with zirconium compounds in a non-oxidizing atmosphere [4].

Here we report the synthesis and microstructural characterization of new EG/coke/ZrC composites produced through the “chemical compression – Zr-cellulose” approach.

Experimental

Expandable graphite was synthesized by anodic polarization of graphite in 60% HNO₃ aqueous solution at a stabilized current of 30 mA with a total electrical charge of 1500 C/g. ZrOC₂O₄-modified cellulose was synthesized as follows: initial microcrystalline cellulose was treated with 70% HNO₃ and then hydrolyzed to form activated cellulose. The hydrolysis procedure was carried out until pH=6-7 of the extract. Activated cellulose was impregnated with ethanol solution containing 15 wt.% of ZrO(NO₃)₂·6H₂O and next treated with 10% H₂C₂O₄ ethanol solution to result in ZrOC₂O₄-modified cellulose.

The composites were prepared using “chemical compression” approach. An intimate mixture of 0.8 g of ZrOC₂O₄-modified cellulose (filament length ~250 μm), 0.64 g of expandable graphite and 0.16 g of phenol-formaldehyde resin (PFR) powder in a sealed metal container of 1.6 cm diameter and 5 cm height was installed into 900 °C heated furnace to provide as fast as possible heating rate (so-called “thermal shock”) and kept there for 2 minutes. In such a way the Zr-modified EG/coke block was obtained which was then

heated at 1550°C for 4 h in nitrogen to result in EG/coke/ZrC composite. The reference Zr-free EG/coke sample was obtained by “chemical compression” of a mixture of 0.64 g of expandable graphite and 0.16 g of PFR powder.

The phase composition of the composites was determined by X-ray diffraction on an ARL X’TRA diffractometer (CuK_α radiation, λ = 1.5418 Å) in the angular range of 2θ = 20°-70° with the steps of 0,02°. Morphologies of the composites were characterized by scanning electron microscopy (SEM) performed on a JEM-5510 instrument coupled with an EDX spectrometer (INCA Energy+, energy resolution below 1 eV). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) experiments were performed on Philips CM-20 microscope at 200 kV. Specimens for TEM were prepared by mechanical grinding in methanol and depositing the suspension on a holey carbon grid.

Results and Discussion

According to X-ray diffraction data (Fig. 1) the phase composition of EG/coke/ZrC composite is represented by graphite and *c*-ZrC. The content of ZrC determined by combustion method is around 11 wt.%. An average size of ZrC crystallites estimated using Sherrer equation comes to 25 nm which correlates with the oxide crystallite size synthesized through metal-cellulose approach [5].

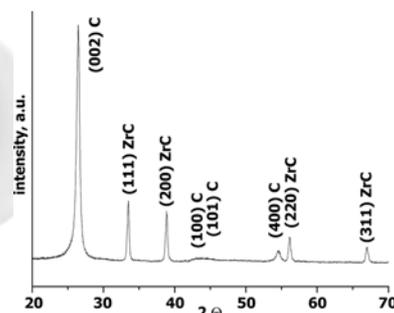


Fig. 1 XRD pattern of the EG/coke/ZrC composite.

ZrC is mostly formed as “sticks” within the EG/coke matrix indicating that the initial cellulose fiber morphology is mostly preserved. The length of these ZrC particles is 30-60 μm, which is 5-10 times lower than that of the initial modified cellulose fibers. The tiny slivers of ~ 1-3 μm size randomly distributed over the whole EG surface are present in the sample as well. Some of them are PFR coke particles as follows from the SEM observations of the Zr-free sample (Fig. 2b), but the majority are the smallest ZrC slivers as confirmed by EDX (not shown in the Fig. 2a). These smallest ZrC particles have sharp boundaries indicating that they are the splinters of the bigger pieces and were formed simultaneously with them.

The observed fiber breaking should be accounted for the mechanical pressure of the carbon matrix during “chemical compression”. When the temperature within the container reaches 250-400 °C cellulose fibers are weakened due to their

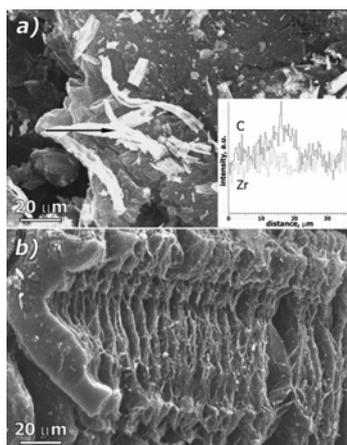


Fig. 2 SEM images of a) the EG/coke/ZrC composite, b) the reference Zr-free sample.

partial decomposition [6] and mechanically destructed in intimate contact with expanding graphite. Water vapour release accompanying cellulose decomposition is also responsible for fiber breaking. The crushing of ZrC particles is a significant process and in the specific experimental conditions it doesn't allow the formation of ceramic network though the majority of the ZrC pieces are characterized by high aspect ratio and locally form the net (Fig. 2a). The convenient enlargement of Zr-modified cellulose portion in the reaction mixture seems to be useful to create an entire network within the carbon matrix.

TEM analysis revealed another type of ZrC objects in the EG/coke/ZrC composite (Fig. 3). These objects appear as blobs of ten nanometers associated into structureless lengthy agglomerates of $\sim 1 \mu\text{m}$ length. The blobs are identified as the *c*-ZrC nanoparticles as confirmed by SAED taken from the area A (Fig. 3, lower panel) which is in agreement with the XRD data (Fig. 1). Thus TEM analysis disclosed the hierarchy in the distribution of ZrC nanoparticles: isolated nanoparticles of $\sim 20\text{-}50 \text{ nm}$ diameter which are gathered in the lengthy dendrite-like structures of $200\text{-}1000 \text{ nm}$.

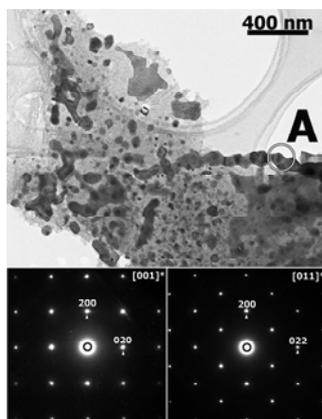


Fig. 3 TEM image of the EG/coke/ZrC composite. The diffraction patterns of the area A are displayed in the lower panel.

We suppose that a process responsible for the ZrC nanoparticles formation and their distribution over the carbon matrix is the emission of gases, preferentially steam and CO_x , caused by a rapid thermal decomposition of the ZrOC_2O_4 -modified cellulose fibers. This dispersive process depends on a heating ramp of the modified cellulose and a total gas pressure inside the container which are influenced by the EG/coke matrix thermal conductivity and the pressure of gaseous products during expansion. Some of ZrC nanoparticles were immobilized by carbon matrix and stay isolated whereas others associate up to dendrite-like agglomerates.

Conclusions

A novel technique of expanded graphite/coke/ZrC composite production using “chemical compression” and Zr-cellulose approaches was developed. ZrC nanoparticles in the composite are associated at three scales: $20\text{-}50 \text{ nm}$ – isolated nanoparticles; $200\text{-}1000 \text{ nm}$ – lengthy dendrite-like structures; $1\text{-}40 \mu\text{m}$ – sticks isomorphous to cellulose precursors.

Acknowledgements

The authors gratefully acknowledge Prof. V. P. Novikov (Scientific-Practical Material Research Center NAS of Belarus, Minsk) for the synthesis of ZrOC_2O_4 -modified cellulose.

References

- [1] Blain PD, Mercuri RA. Thermal insulating device for high temperature reactors and furnaces which utilize highly active chemical gases. US patent 6387462, 2002.
- [2] Rutherford RB, Dudman RL. Ultra-thin flexible expanded graphite resistance heater. US patent 2004086449, 2004.
- [3] Avdeev VV, Semenenko KN, Ionov SG, Litvinenko AYu, Il'inskaya TM, Polovnikov SP, et al. The method of manufacturing porous isotropic graphite articles. SU patent 1617869, 1994.
- [4] Hamling B. Flexivle microcrystalline zirconium carbide fabric. US patent 4162301, 1979.
- [5] Novikov VP, Matveev AT, Viktorov IA, Soroka VO, Bashmakov IA, Tikhonova TF, et al. Metal-cellulose synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. Superconductivity: Physics, Chemistry, Technology 1989;2:178-82.
- [6] Morgan P. Carbon fibers and their composites. Boca Raton FL: Taylor and Francis Group, 2005: 270-272.