Formation of Graphite Materials by Decomposition of Liquid Hydrocarbons Heated to High Temperatures

Dmitrii Karavaev[1] *, *Elena* Matygullina[1], *Lyudmila* Sirotenko[1], and *Felix Raymundo* Saucedo-Zendejo[2]

[1]Department of Innovative Technologies of Mechanical Engineering, Mechanical Engineering Faculty, Perm National Research Polytechnic University, Komsomolsky prospekt 29, 614990, Perm, Russia
[2]Centro de Investigacion en Matematicas Aplicadas, Universidad Autonoma de Coahvila, Unidad Saltillo, Saltillo, Mexico

Abstract. The possibility of forming materials, blanks and products made of graphite by decomposition of liquid hydrocarbons heated to high temperatures has been shown. Optimal modes for growing bulk products in liquid hydrocarbons have been determined. It is presented the Raman spectra of the obtained of graphite materials samples with the signs of presence of carbon nanostructures of various types in these materials.

Introduction

The traditional method of obtaining products from graphite materials is the molding of initial powders into porous blanks and subsequent high-temperature treatment. This method is effective enough for creating small-sized, simple-shaped products. At the same time pressing with subsequent high-temperature exposure does not always make it possible to produce critical structural elements with the required operational properties.

One of the most interesting ways to solve the problem of creating products from graphite materials is the development of fundamentally new additive technologies. However, existing technological developments in this area [1-10] involve the use of binders which often negatively affect the operational properties of products based on these materials.

The aim of this work is to develop an additive technology of 3D printing of monolithic product or billet made of graphite materials by means of its graphitization from liquid hydrocarbons in the process of heating to high temperatures which makes possible to form blanks or products made of graphite materials without binders.

* Corresponding author: karavaev1@ya.ru

Experimental

In the process of obtaining a monolithic product or a graphite billet the parts made of this material are placed in liquid hydrocarbon (transformer oil or industrial oil) and after that one of the rod–shaped parts is connected to the plus of the welding device and the other to the minus (Fig. 1).

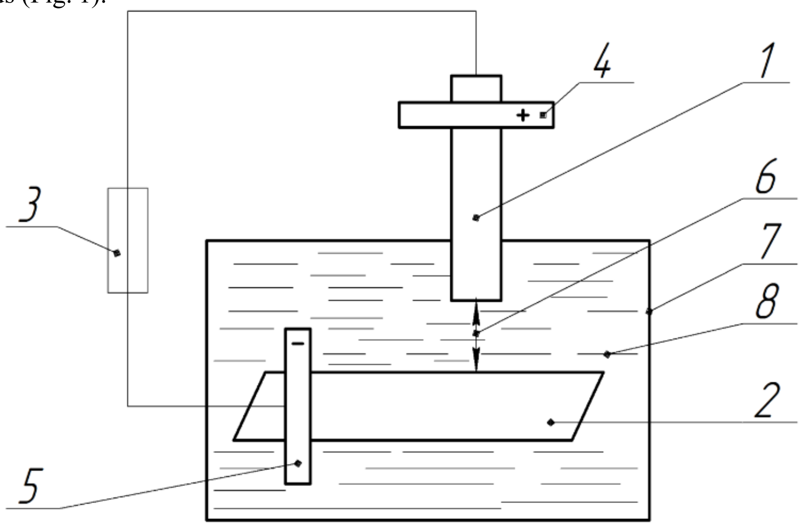


Fig. 1. The process of graphitization from liquid hydrocarbon: 1,2 – graphite parts, 3 – current source, 4 – terminal for connection to plus (+), 5 – terminal for connection to minus (-), 6 – gap between the part-rod and the part-plate, 7 – container for liquid hydrocarbon, 8 - transformer T1500 or industrial oil

In the process of heating the parts to a high temperature, an electric arc is formed between the parts and liquid hydrocarbon evaporation occurs with the formation of carbon on the surface of the parts.

The part connected to the minus is made in the form of a substrate plate. Both parts are placed in a liquid hydrocarbon with a gap under each other. The rod part is installed with the possibility of reciprocating movement in the process of heating in both horizontal and vertical planes relative to the plate part and is heated with a current of 30-60 A. During the heating process it takes place evaporation and dissociation of liquid hydrocarbon which forms a coating of the junction with a layer of carbon material in contact with the surface of the part-plate.

So, in the process of the product formation both parts with the same electrochemical potential are used and at that the rod-shaped part acts as a catalyst for the process, while liquid hydrocarbon is used as the main raw material for the resulting billet or product. The catalytic properties of the rod part accelerate the decomposition of hydrocarbon at lower current and temperature values. The placement of the rod part with a gap above the plate part makes it possible to build up actively the layers of the resulting graphite from liquid hydrocarbon on the substrate.

The translational movement of the rod part to the plate in the vertical plane allows ensuring the arc process of building up the layers of graphite formed from liquid hydrocarbon between the parts. During this process layers of newly formed graphite are deposited on the plate part (substrate for layers). The subsequent vertical movement of the rod part from the plate makes it possible for new portions of liquid hydrocarbon to enter the gap and build up a new layer of graphite on the already formed layer or layers of graphite.

At the same time it is possible to regulate the number of layers necessary to obtain a given size of the billet or product.

The movement of the rod part in the layer build–up zone during reciprocating movement in the horizontal and vertical planes relative to the substrate part, similarly to the 3D printing method, ensures the geometry of a given product. The rod part activates the structure formation of a new material and the connection between the elements of the new structure of graphite from liquid hydrocarbon.

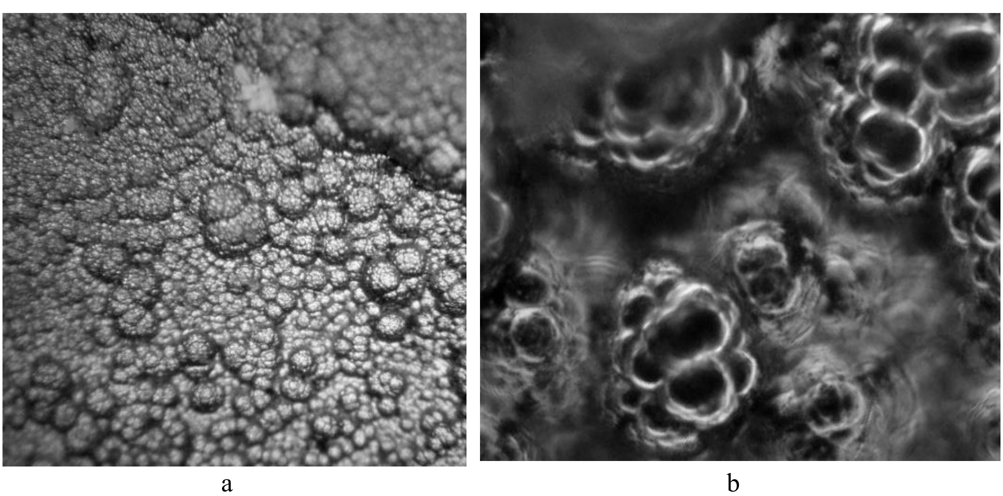
Heating modes (30-60 A) affecting the arc formation process, the size of the gap between the rod part and the substrate in the initial state and during the formation of layers of the formed material on the plate as well as the speed of reciprocating movement during heating in both horizontal and vertical planes relative to the part-plate can be used as technological parameters of this process allowing to control the structure and properties of the newly formed material between the parts (rod and plate).

Results and discussion

As complex experimental studies have shown the effect of increasing graphite layers in the form of tightly packed structural elements and obtaining products from liquid hydrocarbons is achieved using not only graphite electrodes but also copper–copper and nickel-nickel electrodes. Such results indicate the expansion of the capabilities of this method which involves the production of graphite materials in the process of utilization of various metallic and non-metallic materials as electrodes.

The structure of the resulting graphite was studied by an Altami MET 5 optical microscope and a multifunctional Raman spectrometer with Fourier transform Senterra (Bruker, Germany) at a wavelength of 532 nanometers emitting gap and emitter power of 10 mW. The spectra were processed by OPUS 65 software in semi-automatic mode with the Gauss function use.

The results of investigation of the graphite material structure obtained in the process of the build-up during graphitization from transformer oil are shown in Fig. 2.



a b

Fig. 2. Graphite layers obtained in the process of building them up during graphitization from transformer oil T1500 and using graphite-graphite electrodes (a – x 200; b – x 1000)

6 samples with different production conditions were examined (Table 1).

Table 1. Marking of samples

Characteristics of the conditions for obtaining a sample		Marking
Material of electrodes	Current value	
Graphite-graphite, from the substrate	40 A	DMK-1
Graphite-graphite, from the substrate	60 A	DMK-2
Copper-Copper, from the substrate	40A	DMK-3
Copper-Copper, from the substrate	30A	DMK-4
Copper-Copper, from the substrate	50 A	DMK-5
Copper-Copper, from the electrode	40 A	DMK-6

Figure 3 shows the Raman spectra of graphite materials obtained by building up layers of graphite released during the heating of hydrocarbons with graphite (samples No. 1-2) and copper (samples No. 3-6) electrodes utilization.

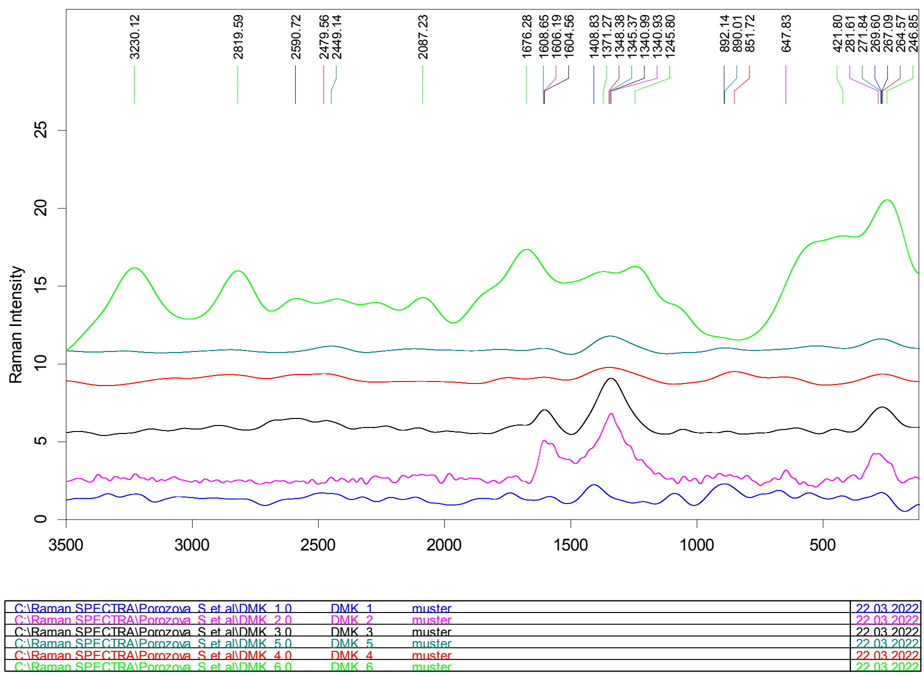


Fig. 3. Raman spectra of graphite materials obtained from hydrocarbons

The Raman spectra shown in Fig. 3 contain a number of characteristic peaks of different intensities with different Raman shifts and geometries. The G–band is located near 1582 cm^{-1} and reflects the degree of crystallization of the material. The D–band is located near 1350 cm^{-1} and reflects the degree of structural disorder near the edge of the microcrystalline structure. It is sufficiently pronounced G and D peaks in the Raman spectra of samples No. 2 and 3, for the rest of the samples these peaks are significantly smoothed and characterized by an increase in their width. Comparison of the Raman spectra presented in Fig. 3 with the results obtained in [11-22] suggests the presence of carbon nanostructures such as nanofibers and nanotubes in the resulting material.

Summary

The result of the research is the establishment of the possibility of forming materials, billets and products made of graphite obtained by decomposition of liquid hydrocarbons such as transformer and industrial oil when they are heated to high temperatures.

Optimal modes for growing bulk products in liquid hydrocarbons have been identified.

In terms of Raman spectroscopy method it has been studied the structural state of the extended layers in liquid hydrocarbons indicating the presence of bands characteristic of carbon nanomaterials in the RAMAN spectra.

References

1. C.W. Hull, Apparatus for production of three-dimensional objects by stereolithography. US Patent, No. 4575330 (1986).

2. R. Singh, V. Singh, Experimental investigations for rapid moulding solution of plastics using polyjet printing. Mater Sci Forum 701. P. 15–20 (2012).

3. C. Zhu, T.J. Han, E. Duoss, A. Golobic, J. Kuntz, C. Spadaccini, M. Worsley, Highly compressible 3D periodic graphene aerogel microlattices. Nature communications, 6, 6962 (2015).

4. D. Lin, S. Jin, F. Zhang, C. Wang, Y. Wang, C. Zhou, G.J. Cheng, 3D stereolithography printing of graphene oxide reinforced complex architectures. Nanotechnology. V. 26(43):434003 (2015).

5. A. Ambrosi, M. Pumera. 3D-printing technologies for electrochemical applications. Chem Soc Rev. 45, P/2740–2755 (2016).

6. R.L.Truby, J.A. Lewis, Printing soft matter in three dimensions. Nature. 540. P. 371–378 (2016).

7. H. He, M. Akbari, L. Sydänheimo, L. Ukkonen, J. Virkki, 3D printed graphene antennas and interconnections for textile RFID tags: fabrication and reliability towards humidity. Int J Antenn Propag. 1–5 (2017)

8. M. Wei, F. Zhang,W. Wang, P. Alexandridis, C. Zhou,G. Wu, 3D direct writing fabrication of electrodes for electrochemical storage devices. J Power Sources 354. P. 134–147(2017).

9. R.M. Hensleigh, H. Cui, J.S. Oakdale, C.Y. Jianchao, P.G. Campbell, E.B. Duoss, C.M. Spadaccini, X. Zheng, M.A. Worsley, Additive manufacturing of complex micro-architected graphene aerogels - Materials Horizons, 5, P. 1035-1041 (2018).

10. Z. Qi, Jianchao Ye, Wen Chen, J. Biener, E. Duoss, C. Spadaccini, M. Worsley, C. Zhu, 3D-Printed, Superelastic Polypyrrole–Graphene Electrodes with Ultrahigh Areal Capacitance for Electrochemical Energy Storage. Advanced Materials Technologies. 3 (2018)

11. A.C. Ferrari, J.C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K.S. Novoselov, S. Roth, A.K.Geimm Raman spectrum of graphene and graphene layers. Phys Rev Lett. 97(18).187401 (2006).

12. A.C. Ferrari, Raman spectroscopy of graphene and graphite: Disorder, electron–phonon coupling, doping and nonadiabatic effects, Solid State Commun. 143 (1–2), P. 47–57 (2007).

13. M.A. Pimenta, G. Dresselhaus, M.S. Dresselhaus, L.G. Cançado, A. Jorio, R. Saito, Studying disorder in graphite-based systems by Raman spectroscopy. Phys Chem Chem Phys. 9(11), P. 1276-1291 (2007).

14. L.G. Cançado, A. Reina, J. Kong, M. Dresselhaus, Geometrical approach for the study of G′ band in the Raman spectrum of monolayer graphene, bilayer graphene, and bulk graphite, Physical Review B. 77 (24), 245408 (2008).

15. M.S. Dresselhaus, A. Jorio, M. Hofmann, G. Dresselhaus, R. Saito, Perspectives on carbon nanotubes and graphene Raman spectroscopy. Nano Lett. 10(3). P. 751-758 (2010).

16. L.G. Cançado, A. Jorio, E.H. Ferreira, F. Stavale, C.A. Achete, R.B. Capaz, M.V. Moutinho, A. Lombardo, T.S. Kulmala, A.C. Ferrari, Quantifying defects in graphene via Raman spectroscopy at different excitation energies. Nano Lett. 11(8)), P. 3190–3196 (2011).

17. I. Childres, L.A. Jauregui, W. Park, H. Caoa, Y.P. Chena, Raman spectroscopy of graphene and related materials, in: New developments in photon and materials research (2013).

18. V. Sharma, D. Uy, A. Gangopadhyay, A. O'Neill, W.A. Paxton, A. Sammut, M. Ford, P. Aswath, Structure and chemistry of crankcase and exhaust soot extracted from diesel engines, Carbon 103, P.327–338 (2016).

19. J.A. Desai, C. Biswas, A.B. Kaul, Inkjet printing of liquid-exfoliated, highly conducting graphene/poly(3,4 ethylenedioxythiophene):poly(styrenesulfonate) nanosheets for organic electronics. Journal of Vacuum Science & Technology. B. Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena, V 35. 03D112 (2017)

20. T. Gupta, Graphene. In: Carbon. Springer, Cham. https://doi.org/10.1007/978-3-319-66405-7_7 (2018).

21. W. Bodnar, M. Schiorlin, A. Frank, T. Schulz, N. Wöhrl, C. Miron, C. Scheu, J. Kolb, A. Kruth, Synthesis of graphene-related carbon nanoparticles from a liquid isopropanol precursor by a one-step atmospheric plasma process. Applied Surface Science. 514. 145926 (2020).

22. https://www.czl.ru/blog/raman-spectroscopy/graphene-raman-analyzer-carbon-nanomaterials-characterization.html