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Syntesis of Carbon Nanomaterials in a Cyclic Reactor Using Buffer Gases

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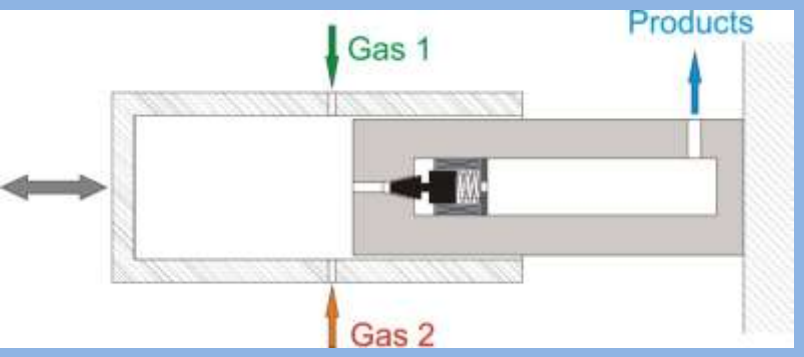
Experimental scheme



Mechanical characteristics
Piston diameter – 47 mm
Piston stroke – 200 mm
Compression ratio – up to 100
Frequency ≤ 10 Hz

Gases
Gas 1 = Hydrocarbons (pure or mixture with inert gases)
Gas 2 = Ar or He

Reaction conditions
TDC pressure ≤12.0 MPa (measured)
Temperature – up to 1800K (calculated)

The calibrated tension gauge was used to measure pressure. The Fig. 1 presents typical pressure-time diagram at different opening modes of the exhaust valve.

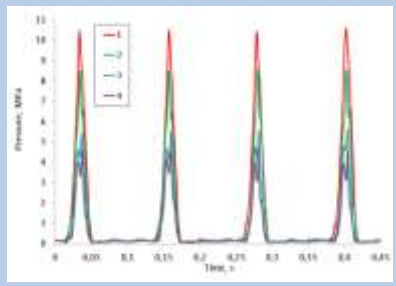


Fig. 1.

The universal gas analyzer UGA-200 was used to measure content of species in precursors and products. The Fig. 2 presents typical product's diagram.

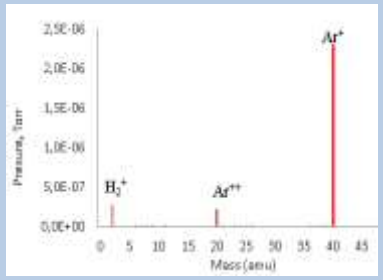


Fig. 2.

Results

CH_4, C_2H_2, C_2H_4, SiH_4 were used as precursors. Carbon nanoparticles (CNs) were produced. CNs were characterized by TEM, SEM and Raman spectroscopy. Also diffraction data were received for CNs.

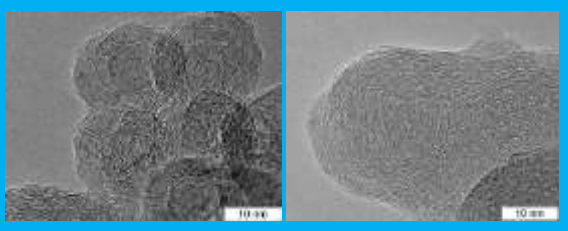


Fig. 3. TEM images of soot globules of carbon nanoparticles with and without internal cavities, synthesized from mixture 5% C_2H_4 + 95% Ar at different pressures: a - 5.5 MPa; b - 8.0 MPa.

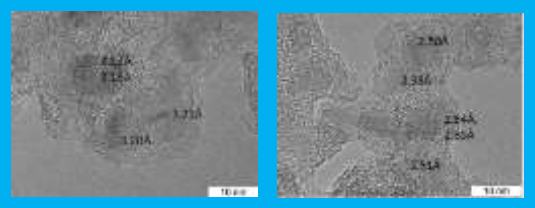


Fig. 4. TEM images of nanoscale crystallites Si with interplanar distance about 3,2Å - (a) and Core-shell particles - SiC 5-10 nm in size coated with carbon 2-5 nm thick with interplanar distance about 2,5Å - (b) were produced at 7.8 MPa from mixture 2.5% SiH_4 + 2.5% C_2H_4 + 95% Ar .

Fig. 5. SEM image of cubic CNs synthesized from mixture 2.5% C_2H_2 + 97,5% He at pressure 5.0 MPa.

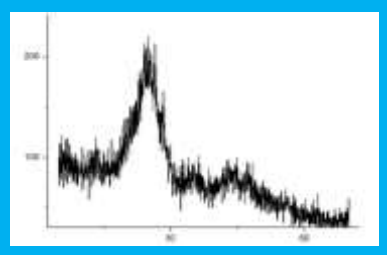


Fig. 6. Diffraction analysis data for CNs synthesized from mixture 5% CH_4 + 95% Ar at 11.0 MPa.

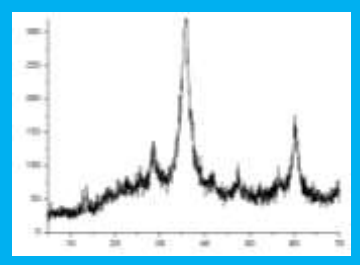


Fig. 7. Diffraction analysis data for CNs synthesized from mixture 5% C_2H_4 + 5% SiH_4 + 90% Ar at 8.0 MPa.

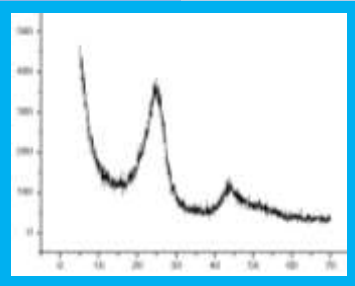


Fig. 8. Diffraction analysis data for CNs synthesized from mixture 25% C_2H_2 + 75% Ar at 5.0 MPa.

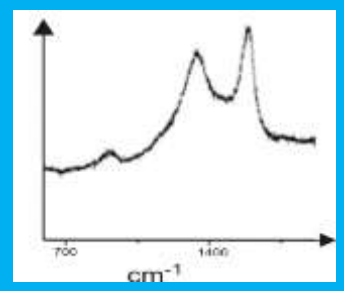


Fig. 9. Raman spectrum for CNs synthesized from mixture 5% CH_4 + 95% Ar at 11.0 MPa.

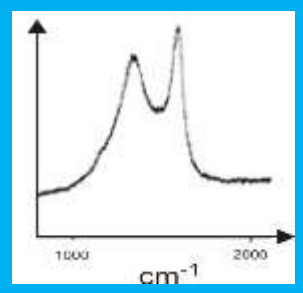


Fig. 10. Raman spectrum for CNs synthesized from mixture 10% C_2H_4 + 90% Ar at 11.0 MPa.

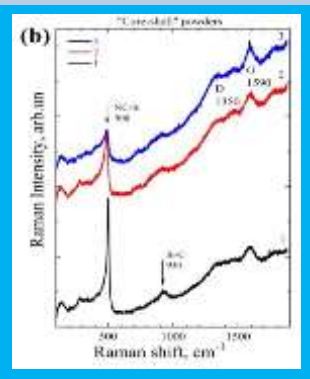


Fig. 11.
Raman spectrum for CNs synthesized from mixture 5% C_2H_4 + 5% SiH_4 + 90% Ar at 6.0 MPa, 8.0 Mpa, 10.5 MPa. [1]

Conclusions

Carbon and carbon-silicon particles were synthesized from methane, ethylene, acetylene and silane. Chemical reactions of pyrolysis of the selected precursors occur at temperature above 1000-1500K. At pressure up to 12.0 MPa such temperature conditions can be obtained in atmosphere of buffer monatomic gases due to the high adiabatic index. The use of argon and helium as buffer gases showed that the higher the molecular weight of the buffer gas the faster the thermodynamic equilibrium between the buffer gas and the precursor is established. In argon atmosphere all substances under study were decomposed almost completely in the operating pressure range, whereas in helium only acetylene with a minimum concentration was decomposed.

The higher the enthalpy of formation the easier precursors were to decompose. Having the minimum enthalpy methane was decomposed in argon at a pressure of 10.0 MPa.

The synthesized carbon nanoparticles had a bulbous structure with or without internal cavities. Diffraction and Raman analyzes show the presence of graphite-like structures.

Decomposition of silane with hydrocarbons also led to the formation of bulbous core-shell nanostructures with silicon or silicon carbide inside that is confirmed by both diffraction and Raman analysis.

The decomposition of acetylene in helium yielded rather large cubic carbon structures more than 200 nm in size. The composition of the structures is currently being investigated.

The compression reactor is showing its applicability for the complete decomposition of simple hydrocarbons to form carbon nanoparticles and hydrogen. Thus, the use of a chemical compression reactor is an effective tool for the gas-phase synthesis of various carbon-containing nanostructures with significantly different morphologies. The method is promising for the industrial production of nanopowders and demonstrates high productivity [2].

1. B. Ezdin, Yu. Pakharukov, V. Kalyada et al. **The novel method of synthesis of nanostructured materials for the enhancing recovery in oil displacement technologies.** //Catalysis today. 2021. To be published.
2. Ezdin, B., Yatsenko, D., Kalyada, V., et al. Data on the structure, chemical state of silicon carbide synthesized by adiabatic cyclic compression in a chemical reactor.// Data in Brief Volume 2020, 104868 DOI: 10.1016/j.dib.2019.104868