

CARBON FOAMS BASED ON COAL TAR PITCH

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Abstract

Due to their unique properties, carbon foams are widely used in various fields, from medicine to space. Research on the using of coal tar pitch as a cheap precursor for the carbon foams production can provide an economical route to the production of light carbon materials. Coal tar pitch, a by-product of coal processing by high-temperature pyrolysis, is a promising precursor for carbon materials due to its high carbon content and low price. The main problem of coal tar pitch using as a polymer matrix for carbon foams creating is that the rheological properties of the pitch usually do not meet the requirements of foaming. This paper gives a review of the properties of carbon foams based on coal tar pitch, coal tar pitch modification methods to obtain carbon foams. It also looks at obtaining and fields of use of non-carbonized, carbonized and graphite carbon foams based on modified coal tar pitch. The choice of the method for producing carbon foams depends on the area of their application; however, preference should be given to environmentally friendly methods that ensure resource conservation and low energy costs.

Keywords: *Coal tar pitch; Modification; Foaming; Carbonization; Graphitization; Carbon foams.*

1. Introduction

Due to their unique properties: mechanical strength, lightness, chemical resistance, thermal conductivity, heat resistance, electrical properties, etc., carbon foams are widely used in various fields, from medicine to space. Coal tar pitch, a by-product of coal processing by high-temperature pyrolysis, is a promising precursor for carbon materials due to its high carbon content and low price.

The development of the carbon foams synthesis on the basis of cheaper raw materials - coal tar pitch, provides an economical way for the production of light carbon materials. This is a stimulating factor for research in this direction. Coal tar pitch is a thermoplastic material, which is a complex heterogeneous system of highly condensed carbo- and heterocyclic compounds and has a set of properties suitable for polymers [1]. It has a number of advantages over classical polymers - lower cost, chemical, and biological resistance.

The main problem of coal tar pitch using as a polymer matrix for carbon foams creating is that the rheological properties of the pitch usually do not meet the requirements of foaming [2]. Therefore, it is necessary to pre-treat the pitch to improve its rheological properties. Pre-treatment of coal tar pitch consists of its modification due to polymerization or polycondensation processes in order to control the viscosity and degree of anisotropy of the pitch [3].

2. Characteristics of carbon foam based on coal tar pitch

Depending on the properties of the pitch precursor and its processing conditions, carbon foams with cardinaly different properties are obtained, which allows them to be used in a wide variety of industries (Fig. 1).

Depending on the conditions of production, non-carbonized, carbonized carbon foams, or graphite foams are formed. According to morphological characteristics, carbon foams may have a closed-cell or an open-cell structure.

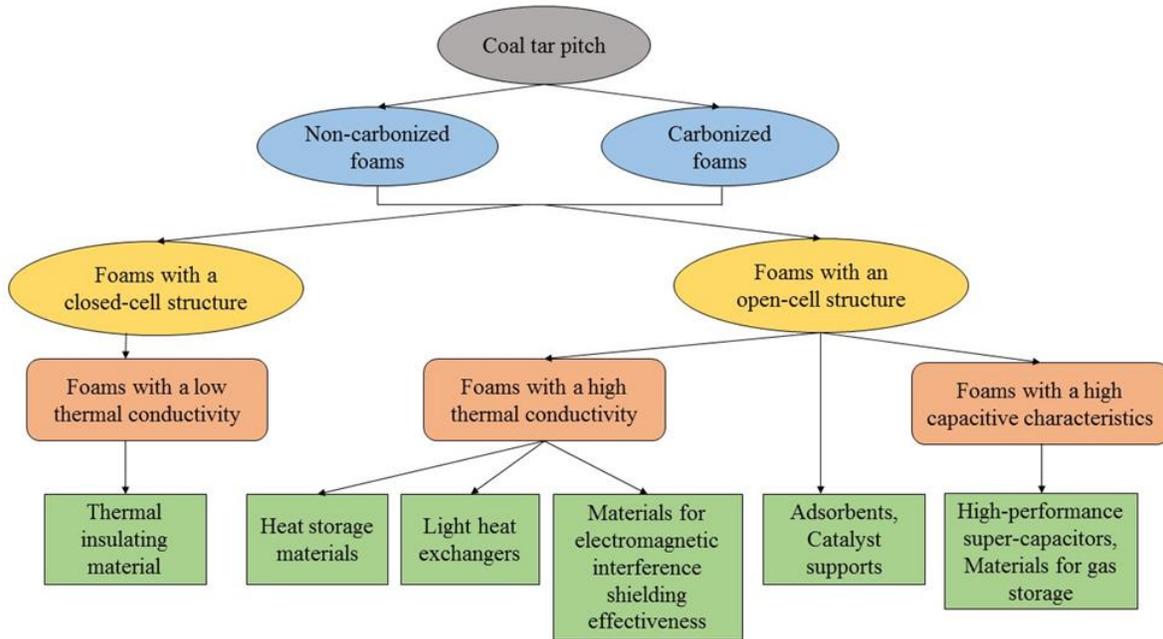


Fig.1. Carbon foams based on coal tar pitch

Carbon foams with a closed-cell structure have low thermal conductivity and are used as a thermal insulation material applied in energy saving buildings [4-7].

Carbon foams with an open-cell structure have a high surface area, which is why they are used as adsorbents for the separation of liquids and gas [8-9], as well as catalyst supports [8-10]. Open-porous carbon foams with high capacitive characteristics are promising for the creation of high-performance supercapacitors [11-13] and materials for gas storage [14]. The high thermal conductivity of such foams allows them to be used as heat storage materials [15], heat exchangers, radiators [10, 16-17], as a personal cooling system for firefighters [18] and materials for electromagnetic interference shielding effectiveness [19-22].

3. Process of carbon foams obtaining

The process of carbon foams obtaining consists of several stages (Fig. 2). The required stage is the pre-treatment of the coal tar pitch by its modification.

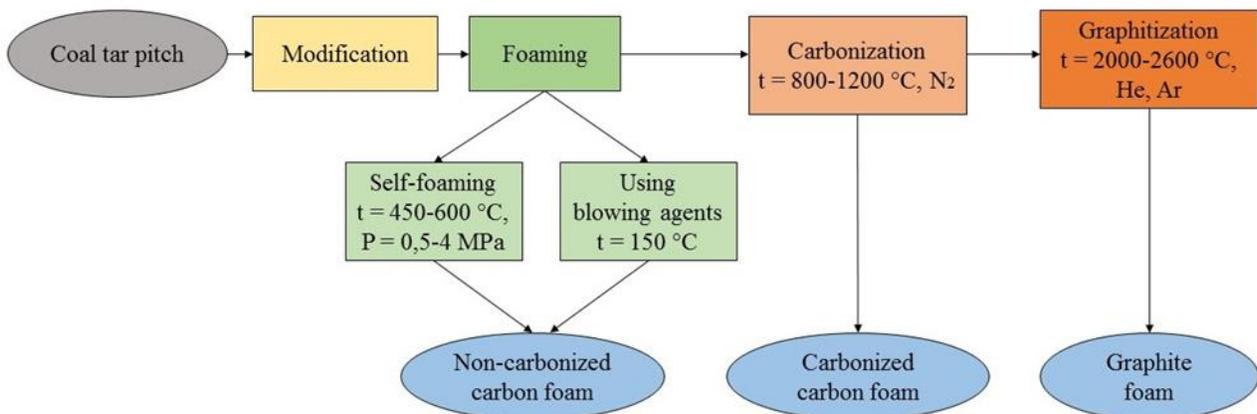


Fig.2. Scheme of carbon foams production

This stage is needed to improve the rheological properties of the pitch. The next stage is foaming the modified coal tar pitch, which is carried out by self-foaming or using blowing

agents. The product of foaming is non-carbonized carbon foam, which is also called as "green" foam. Further carbonization of non-carbonized carbon foam allows obtaining the carbonized carbon foam. The graphitization process converts the carbonized foam into graphite foam.

3.1. Methods of the coal tar pitch modification and foaming

Depending on the method of the coal tar pitch modification, a pitch precursor with certain characteristics corresponding to the requirements of foaming can be obtained. Scheme of modification methods is shown in Fig. 3.

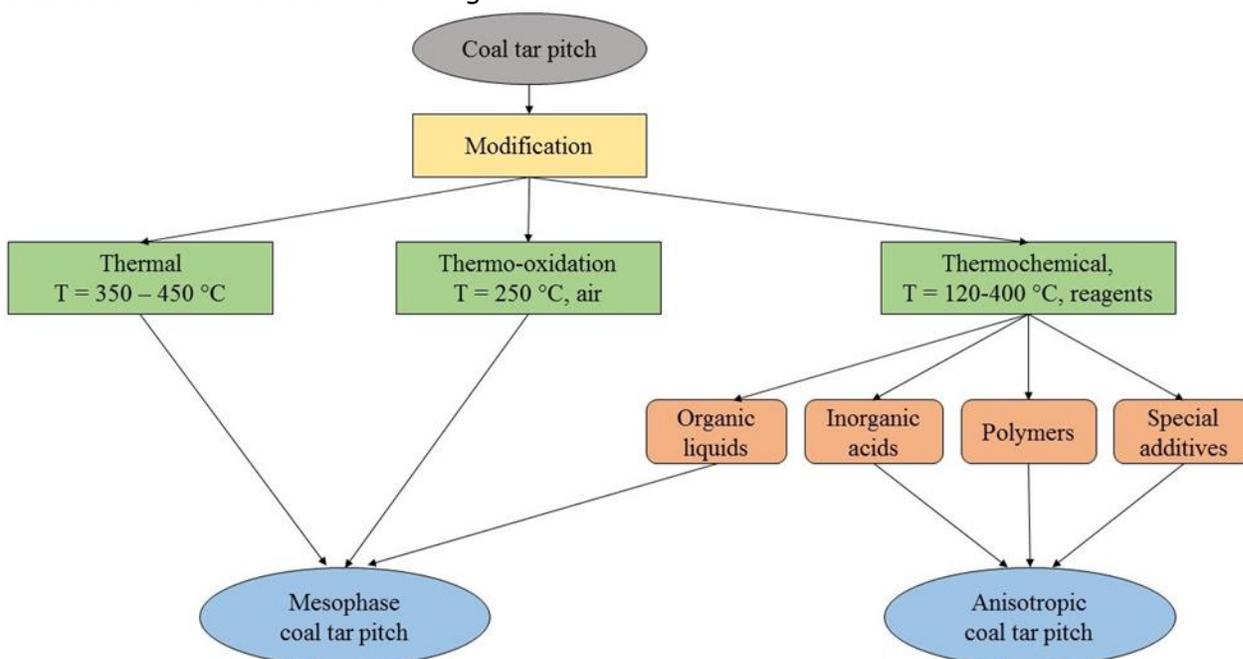


Fig.3. Scheme of coal tar pitch modification methods to obtain carbon foams

Modification of coal pitch may be carried out by thermal, thermo-oxidation, or thermochemical methods. Due to the polymerization and polycondensation processes, the viscosity and softening temperature of the modified coal tar pitch increases, which makes it possible to use it as a precursor to produce carbon foam.

Thermal modification methods are carried out at atmospheric pressure, under vacuum (10 kPa), or under pressure at temperature 350-450°C [4-5,7,10, 15-16,23], producing mesophase pitches. Thermo-oxidation methods involve the use of atmospheric oxygen, which allows reducing the temperature of the pitch modification to 250°C and obtaining mesophase pitches [24-26]. Molecular stitching caused by oxygen function at low temperatures increases the molecular weight of some molecules, preventing their distillation and removal during carbonization.

Thermochemical methods of pitch modification are carried out using various reagents: inorganic acids, polymers, organic liquids, and special additives that convert the coal tar pitch into anisotropic. Thermochemical modification is the most widely used pre-treatment of coal tar pitch for controlled change in the viscosity of the pitch precursor [2,6,8-9,17-18,27-31]. The thermochemical method of modification using organic liquids (tetrahydrofuran) is used to obtain mesophase coal tar pitch [32-33].

Thermochemical modification with inorganic acids H_2SO_4 , HNO_3 [2, 8,9,17-18,27-30] and H_3BO_3 [6] is used by a number of researchers [14,24,34,35] for the pre-treatment of coal tar pitch at temperatures 120-150°C.

Modification of the coal tar pitch by polar polymers (polyvinyl chloride, perchlorovinyl, ethylene vinyl acetate) allows obtaining of anisotropic coal tar pitch [36-38] at temperatures up to 170°C.

The modification of the coal tar pitch with special additives gives the resulting foams the necessary properties for their application in various industries [6,11,14, 27,39]. As additives, ferritic Ni-Zn, Fe, ZnO, silver particles, sawdust, and rosin are used. The modification is carried out in the temperature range of 150-400°C and pressure up to 1.5 MPa.

The foaming of the modified mesophase pitch is carried out by self-foaming at 450-600°C and a pressure of 0.5-4.5 MPa [5,7,23-26]. Pitches modified by polar polymers are foamed with blowing agents [37,40]. At this stage, non-carbonized carbon foams are formed, mainly with a closed-cell structure and low thermal conductivity.

3.2. Carbonization and graphitization stages

After the carbonization stage under the action of high temperatures (800-1200°C) in a nitrogen atmosphere, the carbonized carbon foam is obtained. It has an open-cell structure and has a high specific surface area, high mechanical strength, electrical conductivity, and high capacitive characteristics.

The last stage is the graphitization of carbon foam at a temperature from 2000 to 2600°C in an atmosphere of helium or argon to produce graphite foam. This foam is characterized by an open-cell structure, a high degree of graphitization, high thermal and electric conductivity, a low coefficient of thermal expansion, and a high modulus of elasticity.

4. Obtaining of carbon foams

4.1. Non-carbonized carbon foams

In paper [4], the authors were obtained non-carbonized carbon foam based on coal tar pitch modified by thermal treatment at $t = 450^\circ\text{C}$ in nitrogen protection and keeping this constant temperature for 4 h. Foaming process of carbon foams was carried out in a stainless pressure vessel with increasing the temperature up to 520°C and keeping this constant temperature for 1-8 h. The pressure of the autoclave was 0.4-1.5 MPa. The resulting foam had high compressive strength, low thermal conductivity and can be used as a thermally insulating material.

The authors [23] were investigated the preparation of non-carbonized carbon foam based on modified coal tar pitch. The modification process of the pitch was performed by distillation method at $t = 350^\circ\text{C}$ for 1 hour. Self-foaming of the modified coal tar pitch was carried out at a temperature of 450°C and keeping this constant temperature for 4 hours. Non-carbonized carbon foam had a high compressive strength (up to 6.287 MPa) and low thermal conductivity - lower than $0.048 \text{ W m}^{-1} \text{ K}^{-1}$. Due to these properties, non-carbonized carbon foam can be used as a thermal insulation material.

Non-carbonized carbon foam based on heat-treated coal tar pitch (at 360°C and 10 kPa for 1.5 h) was obtained in paper [5]. Self-foaming of the modified coal tar pitch was carried out using size-restriction method at a temperature of 600 °C for 2 hours. It has been established that due to the uniform pore structure, high compressive strength and low thermal conductivity, the resultant carbon foam can be used as thermal insulation material applied in energy saving building.

The effect of the organic solvent amount on the properties of non-carbonized carbon foams was studied in paper [33]. The process of foam obtaining included the stage of coal tar pitch modification by using 30 wt. % organic solvent and foaming of the modified coal tar pitch at temperature up to 588 K and pressure 3.0 MPa. The authors observed an improvement on the cell densities and mean cell diameters of the carbon foams, depending on the solvent proportions in the process of the coal tar pitch modifying.

Non-carbonized carbon foam can be obtained based on coal tar pitch modified by polar polymers [37, 41-42]. The modification process consisted of heating a mixture of coal tar pitch and polyvinyl chloride at 170°C for 2 hours. Modification [37-38] of coal tar pitch using PVC by low-temperature treatment allows influencing on the softening point of coal tar pitch, its rheological and mechanical properties. Foaming of modified coal tar pitch [41] was carried out by using complex blowing agent [40] (Azodicarbonamide and zinc stearate) at 150°C for 60

minutes. Kinetics study of modified coal tar pitch foaming has shown that using complex blowing agent (CBA) to foam modified pitch depending on its composition allows obtaining solid foams with a porosity of 24 to 76% and an apparent density of 0.31 to 1.0 g/cm³. The obtained non-carbonated carbon foams were characterized by a closed-cell structure and low thermal conductivity, which can be used as a thermally insulating material. The advantages of this method are using sufficiently low temperatures and the absence of any waste, which makes it possible to solve the environmental and energy-saving issues of obtaining carbon foam. There is a reduce in the toxicity of coal tar pitch using modification method by vinyl chloride polymers, in particular, a reduce in the content of carcinogenic components of the coal tar pitch, such as benzo (a) pyrene, etc. [43].

In paper [13], the authors were presented a method for production non-carbonized carbon foams based on coal tar pitch, which was modified and foamed by a one-step microwave-assisted KOH activation. The technological parameters of the process were: a continuous microwave output power of 600 W in a microwave reactor for 30 min in a nitrogen flow. The obtained samples were washed and dried at 383 K for 24 h to obtain the carbon foams. The non-carbonized carbon foam had a surface area of 1786 m²/g, a high specific capacitance of 267 F/g in 6 mol/L KOH aqueous electrolyte at 0.1 A/g and can be used for high performance supercapacitors. The main advantage of this method is the reductions in activation time and KOH dose due to selective heating of granular raw materials by the microwave-assisted activation that leads to a decrease of energy consumption and an increase of the performance ratio to the foam cost.

4.2. Carbonized carbon foams

In work [10], the carbon foam was produced using modified pitches obtained by heat treatment under temperatures from 380 to 450°C, via foaming process into the reaction vessel filled with nitrogen at a temperature of 500°C and pressure of 3 MPa for 2 hours. The resultant green foams were carbonized at 850°C in a nitrogen atmosphere. Carbonized carbon foam had a high compressive strength (from 9.6 to 10.9 MPa), high thermal conductivity, low density, low coefficient of thermal expansion and corrosion resistance. The resulting carbonized foams can be used as heat exchangers and radiators.

A new approach [7] was provided to obtain carbonized carbon foams based on modified coal tar pitch via vacuuming at a temperature from 380 to 420°C and pressure 10 kPa for 2 h. Carbon foams were prepared by self-foaming method under the conditions of normal pressure and 600 °C, subsequently, carbonized at 800°C for 2h. Results indicate that the optimum softening point of modified coal tar pitch are about 292°C and the resultant carbon foam exhibits excellent performance, such as uniform pore structure, high compressive strength (4.7 MPa), low thermal conductivity (0.07 W·m⁻¹·K⁻¹). This kind of carbonized carbon foam is a potential candidate for thermal insulation material.

In papers [24-26], carbonized carbon foams were obtained from coal tar pitches modified by air-blowing at 250°C for 18-14 h. Carbon foams were prepared by self-foaming method at 600°C for 30 min; then the resultant green foams were carbonized at 1000°C. The pitch modification by air-blowing for obtaining carbonized carbon foam produces a significant increase in carbon yield, improved microcrystalline structure and high thermal conductivity of the foams. These properties provide possibilities to use a carbonized carbon foam in the production of heat exchangers and as thermal energy storage materials.

The authors [32] were investigated the preparation of carbonized carbon foam based on coal tar pitch modified by tetrahydrofuran, and then the mixture was sonicated. Thereafter, the sample was foamed and carbonized at different temperatures such as 600°C, 700°C, and 800°C for 1 h under N₂ atmosphere. The carbon foam obtained by this method had an open-cell structure and superior capacitive performance, indicating great potential for practical applications as supercapacitor electrodes. The advantages of the proposed synthesis are sufficient simplicity and efficiency of production.

The goal of the study [8-9] was the development of carbonized carbon foams derived from coal tar pitch modified at 120 °C with concentrated mineral acids – 98% H₂SO₄ or 68% HNO₃.

The foaming process was carried out by heating the pitch up to 600 °C in an N₂ atmosphere for 30 min. The obtained "green" foams were pyrolyzed at 800°C in N₂ atmosphere (heating rate 15°C min⁻¹) and subsequently steam activated for 60 min at the same temperature. The resulting carbonized carbon foams had 89% of the open-cell structure, a porosity up to 70%, high compressive strength (17.4 MPa) and chemical resistance. These porous features along with the high mechanical and chemical resistance of the carbon foams open up new perspectives in the performance of carbon foams, such as their application as adsorbents in the liquid [2] and gas phases [27], as well as catalyst supports in advanced processes for wastewater remediation [28,39].

Carbonized carbon foams were obtained by authors [6] using coal tar pitches modified with cinnamaldehyde and boric acid at 150°C with soaking time of 3 h under an N₂ flow. The foaming process was carried out in a stainless autoclave at 500°C (heating rate 1.5°C/min) for 2 h in an N₂ atmosphere at pressure up to 3 MPa. Then the resultant green foams were carbonized at 800°C in an N₂ atmosphere for 2 h. The resultant carbonized carbon foams had a closed-cell structure, and the highest mechanical strength reaches to 21.3 MPa, which allows to use them as high-temperature thermal insulation.

Carbonized carbon foam with a high specific surface area for the production of supercapacitors was obtained [11] from the coal tar pitch modified with sawdust (ratio of 67 % CTP and 33 % sawdust) at 150°C. After foaming the modified pitch at 500 °C under a nitrogen atmosphere for 2 hours, the resulting foams were carbonized at 800°C for 2 h, followed by KOH activation. The carbonized carbon foams had a high specific surface area of 2224 m²/g, and a favorable specific capacitance of 251 F/g at a current density of 0.5 A/g in 6 mol/L KOH electrolyte. The main advantage of this route of carbonized carbon foam production is reducing the cost of producing electrode materials for supercapacitors.

The authors were investigated [14] the carbonized carbon foams based on coal tar pitch modified with rosin. The copolymerization of pitch and rosin was carried out at 150°C for 30 minutes in a stream of nitrogen. Co-pyrolysis product of coal-tar pitch and rosin was foamed at 450°C under a nitrogen stream and kept for 2 h. The resulting foam was heated in a nitrogen atmosphere until the desired carbonization temperature and maintained under these conditions for 1–2 h, followed by KOH activation. The study showed that adding rosin results in the porosity development in the carbonized carbon foams. The effect of adding rosin on the porosity characteristics of the ACs can be illustrated by increases in the surface area from 1846 to 2847 m² /g and the total pore volume from 1.09 to 1.57 cm³/g. This foam can be used as a material for gas storage and electric double-layer capacitors.

4.3. Graphite foams

In paper [15] was investigated the method of obtaining graphite foams from coal tar pitch, modified at 430°C. Foaming and carbonization of the modified pitch was conducted in a nitrogen atmosphere at a temperature of 1000°C and soaked at this temperature for 1 h. Finally, the foams were graphitized in a helium atmosphere at 2600°C and soaked at this temperature for 1 h. The graphite foams had a bulk density of 0.249 g/cm³, a compressive strength of 0.46 MPa and thermal conductivity of 21 W · m⁻¹ K⁻¹, which allows to use them as thermal energy storage materials.

The authors [16] were proposed to obtain graphite foam from coal tar pitch modified by heat treatment at t=430°C in high pressure and temperature chamber. The foaming process was carried out at a temperature of 450°C and at a pressure up to 4 MPa for 1–4 h. Thereafter, the foam was carbonized at 1200°C with a flow of nitrogen and maintained for 3 h. The carbonized foam was graphitized at 2600°C for 10 min. The porosity of resulted foam was from 55% to 85%, the graphitization degree of foam reaches to 84.9%. The crystallinity of foam gives it useful characteristics including dimensional stability, a low coefficient of thermal expansion, relatively high modulus of elasticity and compressive strength, and very high thermal conductivity. The high porosity and opening give the graphitic foam efficient heat transfer for any working fluid passing through it, which allows using of graphite foam as lightweight heat exchangers.

In papers [17-18, 29-30], the authors have obtained graphite foams from coal tar pitch modified with acids H_2SO_4 and HNO_3 . Foaming of the modified coal tar pitch was carried out at $550^\circ C$ in a nitrogen atmosphere. The resulting "green" foams were carbonized at $1000^\circ C$ in a nitrogen atmosphere and then graphitized at $2000^\circ C$ in an argon atmosphere. Studies have shown that graphite foams had a high thermal conductivity and open porosity, which allows to use them as heat exchangers and a personal cooling system for firefighters.

4.4. Carbon foams with special additives

The composite carbon foam with Ni-Zn ferrite as an additive has been developed by authors [19] for electromagnetic interference shielding. Production of carbon foams was included a modification of coal tar pitch with Ni-Zn ferrite, then the resulting mixture was foamed and the green foams were carbonized at $650^\circ C$ with a soaking time of 2 h in N_2 atmosphere. The authors were observed that the electromagnetic interference shielding effectiveness and the conductivity is enhanced along with the increase of Ni-Zn ferrite additive amount.

The authors [21,44] were investigated the electromagnetic interference shielding effectiveness of carbonized carbon foam filled with silver particles. Modification of coal tar pitch and silver particles as a filler was conducted under an average pressure of 1.5 MPa. Afterwards, the modified pitch was foamed by curing of the molded powder mixtures at temperatures from 120 to $160^\circ C$ for 2 h. After foaming, the green foams were carbonized at $1200^\circ C$ in a flowing argon environment, maintained under these conditions for 2 h. The carbonized carbon foam showed an open porosity of 63-67%, the compressive strength of 13.3–19.5 MPa and pore size distribution of 10–500 μm . It was observed that the addition of silver significantly enhanced both conductivity and shielding effectiveness due to this the carbon foam had unique opportunities for future surface tailoring required in various commercial and aerospace fields.

In papers [20,22,27], the influence of nanosized iron particles on the properties of light weight carbon foam was investigated. After modification the mixture of coal tar pitch with ferrocene at a temperature of $400^\circ C$ for 25 h, the obtained modified coal tar pitch was foamed, carbonized and then graphitized at $2400^\circ C$ in an inert atmosphere. The authors [27] were found that graphite foam had an excellent open-cell structure, a thermal conductivity of $60 W \cdot m^{-1} \cdot K^{-1}$ with a compressive strength in the range of 3.0 - 5.0 MPa. The higher value of conductivity has a positive effect on the electromagnetic interference shielding effectiveness of the carbon foam. The electromagnetic interference shielding effectiveness increased with increasing nanosized iron particles content in carbon foam.

A number of studies [13,19-22,44] show that carbon foams with various additives have significantly higher conductivity, a highly developed open-cell structure, and excellent energy storage performance.

5. Conclusion

Literature analysis has shown that the coal tar pitch can be used as a precursor for carbon foams creating only after its pre-treatment because rheological properties of the pitch do not meet the foaming requirements. Pre-treatment of coal tar pitch consists of its modification due to thermal, thermal-oxidative or thermochemical methods, which allows improving its rheological properties.

Depending on the pitch precursor properties and its processing conditions, carbon foams with cardinaly different properties are obtained: non-carbonized, carbonized carbon foams or graphite foams with a closed-cell or open-cell structure, which allows them to be used in a wide variety of industries.

Non-carbonized carbon foams have a closed-cell structure, low thermal conductivity and can be used as a thermal insulation material. The advantage of the non-carbonized foam production is a quite low temperature of its production. Carbonized carbon foam has an open-cell structure, a high specific surface area and mechanical strength, an electrical conductivity and a high capacitive characteristic. Due to its properties, carbonized carbon foam can be used for the creation of high-performance supercapacitors, adsorbents and catalyst supports.

Graphite foam has an open-cell structure, a high graphitization degree, very high thermal and electrical conductivity, a low coefficient of thermal expansion, and relatively high modulus of elasticity. All of this gives graphite foams unique opportunities for future surface tailoring required in various commercial and aerospace fields.

Carbon foams with special additives have significantly higher electrical conductivity, highly developed open-cell structure, and excellent storage performance. Such foams have a unique opportunity to use them as materials for electromagnetic interference shielding effectiveness. So, research on the using of coal tar pitch as a cheap precursor for the carbon foams production can provide an economical route to the production of light carbon materials. The choice of the method for producing carbon foams depends on the area of their application; however, preference should be given to environmentally friendly methods that ensure resource conservation and low energy costs.

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