

**THE EFFECT OF BORON NITRIDE AND BORON
CARBIDE ADDITIVES ON THE PROPERTIES OF
MESOPHASE PITCH BASED CARBON FOAM**

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PREFACE

This present study consists of production of carbon foam from mesophase pitch by the addition of boron nitride and boron carbide, and also includes production of carbon foam under different temperatures. Also, in this study production of carbon foam from different mesophase pitches of which have different softening points is investigated. Characterization of all samples investigates the effect of parameters to properties of carbon foam.

By the appropriate addition of different ceramic materials to carbon foam, the properties of carbon foam will be much more adjustable and therefore, the carbon foam technologies will make progress in times to come.

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ABBREVIATIONS

SEM	: Scanning Electron Microscopy
C-Foam	: Carbon Foam
BN	: Boron Nitride
B₄C	: Boron Carbide

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THE EFFECT OF BORON NITRIDE AND BORON CARBIDE ADDITIVES ON THE PROPERTIES OF MESOPHASE PITCH BASED CARBON FOAM

SUMMARY

Carbon is a very important element for all living things on Earth. We, all, are made up of organic compounds which are composed of carbon network. Carbon foam is one of the important examples of the new carbon materials. Carbon foam is widely used in many industrial areas.

In commercial category carbon foam used as composite tooling, abrasive tools, battery and fuel cell electrodes, brake disks, engine components, catalytic converters, heat exchangers, energy absorbing crash barriers, structural insulated panels, high temperature insulation, fire doors and blocks, bone surgery material and tooth implants.

In this study, the effects of boron nitride and boron carbide as an additive in the production of carbon foam are studied. Mitsubishi AR, mesophase pitch is selected as the precursor for carbon foam production. Boron nitride, which is 95 % pure, is used. The samples are prepared by using 100 % mesophase pitch and three different additive ratios; 0.1 %, 1 % and 10 % boron nitride and boron carbide. Also, foam is produced from different mesophase pitches of which have the property of different softening points. In addition to these, finally, carbon foam is produced at different temperatures of 300°C, 310°C, 320°C. These samples are heated up to 300°C, and 68 bar pressure is given to the system. The produced carbon foam is stabilized with dry air at 310°C before the carbonization step which is done at 1050°C. To characterize the properties of produced carbon foams, the following steps are examined: Density measurement, scanning electron microscopy (SEM), and compressive test. The characterization steps showed that the best quality is obtained with 100 % mesophase pitch. The structure is negatively impacted with increasing ratio of boron nitride.

The structures and properties of the produced carbon foams are investigated with respect to the parameters involved and further using the characterization results. The parameters investigated are foaming temperature, addition of ceramic materials boron nitride and boron carbide and pitches having different softening points.

As a result of these experiments it is found that; more homogenous, interconnected, better structured, higher density, higher compressive strength and higher porosity carbon foams are derived with increase in temperature.

BOR NİTRÜR VE BOR KARBÜR KATKI MALZEMELERİNİN MEZOFAZ ZİFT BAZLI KARBON KÖPÜĞÜNÜN ÖZELLİKLERİNE ETKİLERİNİN İNCELENMESİ

ÖZET

Yeni ve ileri karbon malzemelerin miktarı her geçen yıl hızla artmaktadır ve bu malzemeler bir çok yeni teknolojinin üretiminin yanında var olan teknolojilerin de daha kolay ve iyi sonuçlar vermesinde çok önemli rol oynamaktadırlar.

Karbon köpüğü bu malzemeler için iyi bir örnektir ve bir çok potansiyel endüstriyel kullanım alanı bulunmaktadır. Karbon köpüğün kullanım alanları iki ana başlık altında incelenebilir. Uçak, Uzay ve Savunma endüstrilerinde karbon köpüğünün kullanım alanları termal koruma sistemleri, ısı transfer sistemleri, uydu antenleri, düşük ağırlıklı zırh, radar gizleme malzemeleri, optik benç ve hafif aynalar olarak sıralanabilir.

Ticari olarak karbon köpüğü kullanımı; kompozit malzemeler, yakıt pili elektrotları, pil elektrotları, makine bileşenleri, katalitik konvertör, yüksek sıcaklık yalıtım, yapısal yalıtılmış paneller, fren balataları, yangına dayanıklı malzemeler, diş implant, kemik protezleri, enerji absorblayıcı ve engelleyici bariyerler, ve aşındırıcı aletler olarak sıralanabilir.

Karbon köpüğü 1960'lerden beri değişik malzemelerden üretilmektedir. Mezofaz ziftten elde edilen karbon köpüğünün popülaritesi özellikle açık gözenek yapısı, yüksek ısıl iletkenliği ve düşük yoğunluğundan dolayı diğer karbon malzemelere nazaran artış göstermiştir. Yüksek ısıl iletkenliğine sahip karbon köpüğünün uygulamaları konusundaki çalışmalar henüz başlangıç aşamasındadır.

Yapılan bu çalışmada, Mezofaz zift bazlı karbon köpüğünün üretilmesinde uygulanan proses şöyledir; mezofaz zift alüminyum kalıba koyulur ve otoklava yerleştirilir. Burada erime noktasının üzerine kadar ısıtılır, sisteme basınç verilir. Basıncın hızlıca boşaltılmasıyla sağlanan içinden bağlantılı gözenekli yapı elde edilir. Daha sonra sırasıyla stabilizasyon ve karbonizasyon yapılması ile karbon köpüğü ele geçirilir. Bu yöntemle elde edilen karbon köpüğü stereo mikroskop, Taramalı elektron mikroskop, cıva porozimetre ve sıkıştırılabilirlik testi ile karakterize edilir. Üretilen karbon köpüklerinin yoğunlukları ölçülmüştür.

Karakterizasyon sonuçlarına göre ise değişik proses şartlarında üretilen karbon köpüğünün yapısı belirlenmiş olur. Bu çalışmada değişik sıcaklıklar, bor nitür ve bor karbür katkıları ve farklı yumuşama noktalarındaki ziftlerin kullanılması ile karbon köpüğü üretimi deneyleri gerçekleştirilmiştir.

Yapılan deneylerin sonucunda, artan sıcaklıkla daha homojen, yoğun, dayanıklı ve gözenekli karbon köpüğü elde edilmiştir.

1. INTRODUCTION

Science and technology has been working to find out new materials which have special properties. The carbon foam is an attractive alternative material to traditional materials in many applications due to its unique properties such as high thermal conductivity, low density, high strength and a porous structure. Carbon foam has been commercially fabricated after 1990's in the world. C-foam Co. and Pocofoam Co. are the best-known companies that produce and market the carbon foam in United States of America.

A relatively simple technique for fabricating extremely high thermal conductivity carbon foams has been developed at Oak Ridge National Laboratory. ORNL first identified the potential of carbon foams for uses in enhancing heat transfer. The technique produces mesophase pitch-based graphitic foam with extremely high thermal conductivity and an open celled structure. The cell walls are made of oriented graphitic like planes, similar to high performance carbon fibers. In fact, it is estimated that the thermal conductivity of the cell walls is greater than 1500 W/m·K (copper is 400 W/m·K). Moreover, due to the low density, the specific conductivity of the foam is over 5 times that of copper and over 4 times that of aluminum.

The open porosity yields a relatively large specific surface area ($>20 \text{ m}^2/\text{g}$), improving heat transfer to a working fluid. This could lead to extremely efficient and lightweight heat exchangers (i.e. air conditioners can be reduced in size dramatically). In fact, when utilized as an evaporative cooling substrate, water can be used as the refrigerant to achieve temperatures below freezing, replacing ozone-depleting freons with a truly environmentally friendly material.

2. THE PROPERTIES OF CARBON AND CARBON FOAM

2.1. Carbon

Carbon is a very important element for all living things on Earth. We, all, are made up of organic compounds which are composed of carbon networks. Carbon is widely distributed in nature. It is found in abundance in the sun, stars, comets, and atmospheres of most planets [1].

Carbon is the sixth element of the periodic table which is shown with the symbol C. Having an atomic number of 6, the electron distribution of carbon is $1s^2 2s^2 2p^2$ [2]. It is also well known that Carbon atoms can have three different hybrid orbital, sp^3 , sp^2 and sp , giving a variety of chemical bonds. This variety makes possible an enormous number of hydrocarbons, from which a great number of organic materials can be constructed. The C – C bond using sp^3 and sp^2 hybrid orbitals was known in the construction of diamond and graphite, respectively, in carbon materials, which are inorganic materials [1].

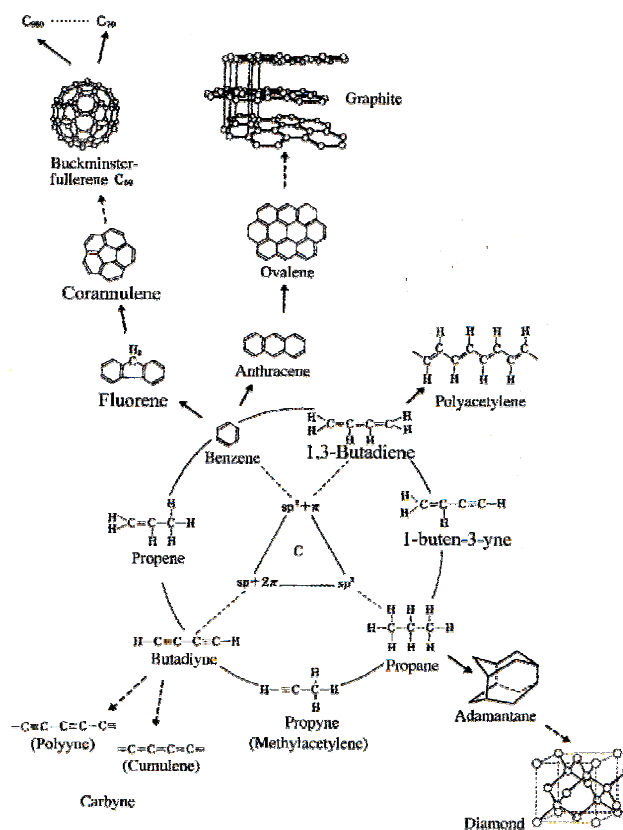


Figure2.1: The large family of carbon materials [1].

Figure 2.1 illustrates how the variety in the bonding nature of carbon atoms leads to a large family of organic molecules and that the inorganic carbon materials, diamond, graphite, fullerenes and carbene, have resulted from extensions to become giant molecules of these organic materials.

Carbon is found free in nature in many different forms called allotropes such as diamond, graphite, amorphous and fullerenes. Due to their different structures allotropes show different physical and chemical properties [1].

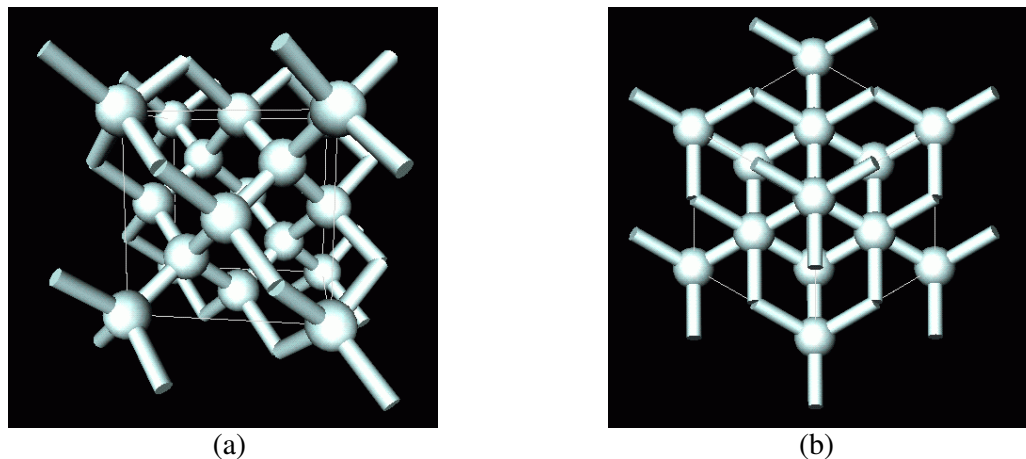


Figure 2.2: The crystal structure of diamond from two different points of view (a) and (b).

Diamond consists of sp^3 orbitals, where chemical bonds extend in three – dimensional space and are purely covalent. It is very hard because of its covalent bonds and is an electrical insulator because of the high localization of the electrons. Long – range periodical repetition of this bond forms diamond crystal.

Graphite consists of sp^2 bonding. In graphite the layers of hexagons of carbon atoms bound using sp^2 orbitals are stacked in parallel using π electron clouds with a regularity of ABAB..., which belongs to the crystal system. Graphite has a typical layered structure and, in consequence, very strong anisotropy in its properties, e.g. very easy cleavage along the layer, and an electrical conductivity that is high along the layer but very poor perpendicular to the layer.

Graphite is black, softer than diamond and conducts electricity. Moreover, in graphite, the atoms form planar, or flat, layers. Each layer is made up of rings containing six carbon atoms. The rings are linked to each other in a structure that resembles the hexagonal mesh of chicken wire. Each atom has three σ bonds (with

120° between any two of the bonds) and belongs to three neighboring rings. The fourth electron of each atom becomes part of an extensive π bond system. Graphite conducts electricity, because the electrons in the π bond system can move around throughout the graphite. Bonds between atoms within a layer of graphite are strong, but the forces between the layers are weak [2].

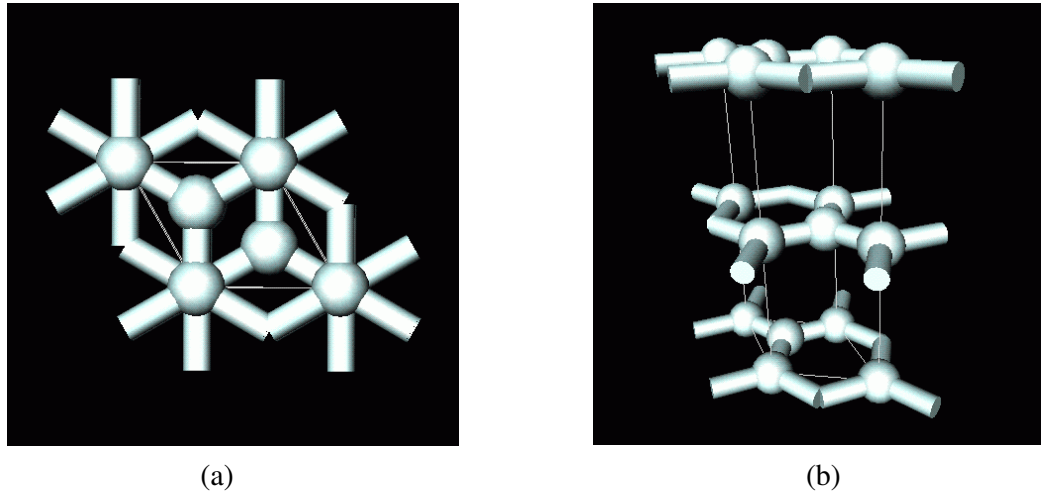


Figure 2.3: The crystal structure of graphite from two different points of view, (a) and (b).

Amorphous carbons are charcoal, coke, anthracite, bituminous coal, lignite etc. They are actually made up of tiny crystal-like bits of graphite with varying amounts of other elements, which are considered impurities. For example, the coal industry divides coal up into various grades depending on the amount of carbon in the coal and the amount of impurities. The highest grade, anthracite, contains about 90% carbon. Lower grades include bituminous coal, which is 76% to 90% carbon, sub bituminous coal, with 60% to 80%, and lignite, with 55% to 73% [3].

A new class of carbon compounds has recently been discovered which are called fullerenes. The original fullerene forms molecules of 60 carbon atoms (with a molecular formula of C_{60}), shaped like tiny soccer balls, with an atom at each point where the lines on a soccer ball would normally meet. Fullerene is used in many ways such as they conduct electricity with no resistance and used as superconductors [4].

Besides these, carbon can also be divided into two groups one of which is graphitizable carbon, and the other is non-graphitizable carbon. The resources of high-quality natural graphite are limited to Sri Lanka, Madagascar and China [1].

Natural graphite is a mineral consisting of graphitic carbon regardless of its crystalline perfection. Synthetic graphite is a material consisting mainly of graphitic carbon, which has been obtained from hydrocarbons at high temperatures. In addition graphitic carbons are all varieties of substance consisting of the element carbon in the allotropic form of graphite irrespective of the presence of structural defects [5].

Non-graphitizable carbons are those, which cannot be transformed into graphitic carbon solely by heat treatment up to 3000°C under or low pressure. Graphitizable carbons are those, which are so converted [3].

Graphitizable carbons have more-ordered structures that lead to little energy requirement to slide graphitic layers over one another. Less-ordered structures need high energy to go graphitic layers. On the other hand, much of the less-ordered parts of the structure are aliphatic in nature, while more-ordered structures have highly aromatic compounds [4]. Figure 2.4 shows the development of long-range order on graphitization.

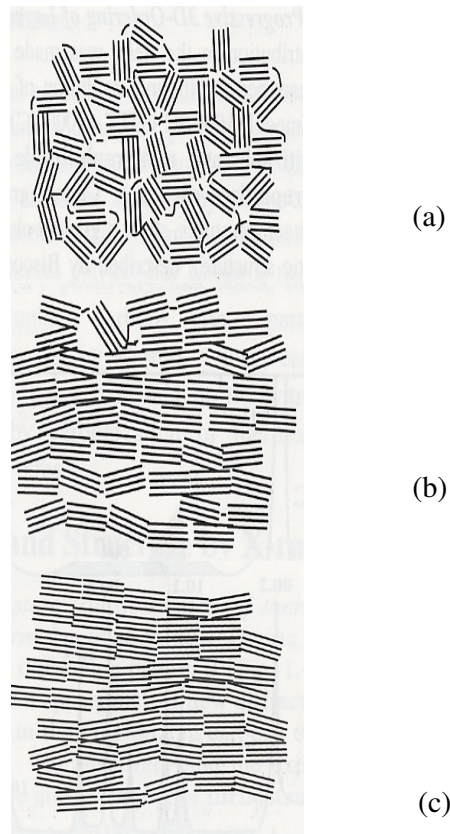


Figure 2.4: Non-graphitizable (a), partially graphitizable (b), graphitizable (c) models of carbon structures [5].

Graphitizable structures are called anisotropic carbons while non-graphitizable structures are called as isotropic carbons.

Anisotropic carbons have essentially approximately parallel arrangements of lamellae, which subsequently assumed increased order during heat treatment to give graphitic structure. Anisotropic carbons are generated from mesophase pitch derived from aromatic hydrocarbons such as naphthalene, petroleum pitch or coal tar pitch [6].

Isotropic carbons have lamellae arranged randomly with associations of small number to give an indication of short-range order, (Figure 2.5). Isotropic carbons are generated from polymeric materials, e.g. cellulose or lignin components in wood.

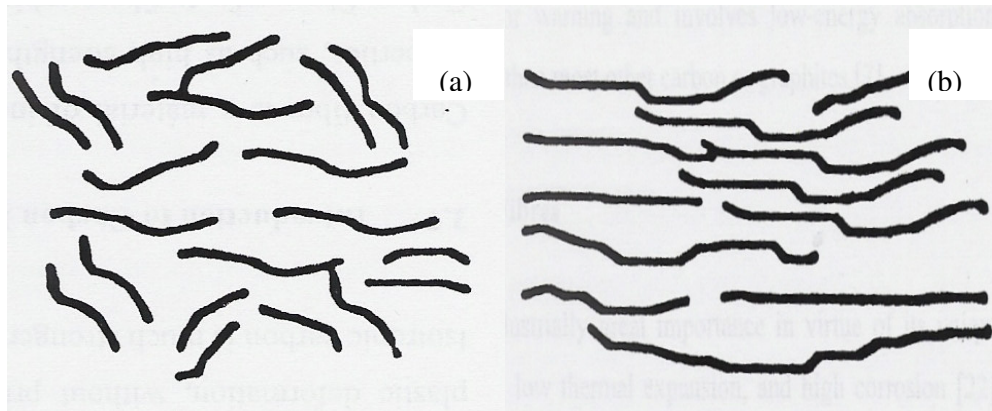


Figure 2.5: (a) Isotropic Carbon, (b) Anisotropic Carbon [7].

2.2. Carbon Foam

Carbon foams were first developed in the late 60's [8]. These initial carbon foams were obtained by the carbonization of foams of plastic materials, such as phenolic resins and polyurethanes. The production of a low density, open celled microcellular carbon foam starts up with the application of high pressure, the sample is then heated. At a specified temperature, the pressure is released, thus causing the liquid to foam as volatile compounds are released. The polymeric precursors are cured and then carbonized without an oxidative stabilization step [9, 10, 11]. These precursors produce "glassy" or reticulated vitreous carbon (RVC) foams, which are attractive for many aerospace and industrial applications, including thermal insulation, impact absorption, acoustic control, catalyst support, and metal and gas filtration. They are thermally stable, low in weight and density, and are chemically pure; they have low thermal expansion, resist thermal stress and shock, and are relatively inexpensive

[12]. In the 1970's, researches focused primarily on producing carbon foams from alternative precursors, various processing and precursor changes in an attempt to modify properties and reduce cost.

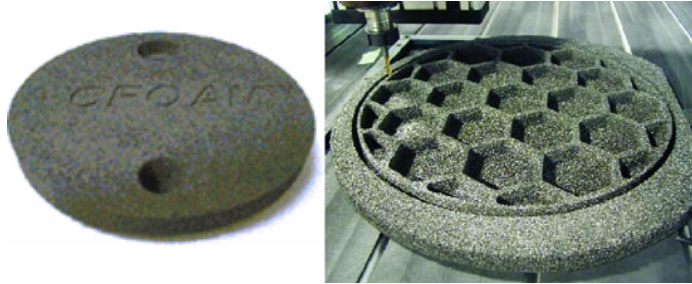


Figure 2.6: The photographs of carbon foam [13].

Carbon foams are often conveniently classified as closed cell foams or open cell foams. When the holes of the foam are connected to one another, the structure is defined as “Open cell foams”, and “closed cell foams” while the holes are isolated within the mass [14].

Carbon foam can be made from a variety of precursors. The precursor and the process determine the properties of the foam; therefore carbon foam is a tailorable material.

The density of carbon foam is ranging from 0.20 g/cm^3 to 0.7 g/cm^3 . Carbon foam has highly porous structure and has uniform distribution of pore sizes (average between 10 and 500 microns), usually contain very little closed porosity, and at least 90% of the pores are open [14]. However, deviations from these preferable properties are possible by changing the operating conditions and the precursor [15]. For example, varying the pressure applied, the size of the bubbles formed during the foaming will change, beside the density and strength; moreover other properties can be affected [16].

Other unique property of carbon foam is its tailorable thermal conductivity [17]. The thermal conductivity of carbon foam depends on applied temperature, and precursor. For example, if carbon foam is heated to $1000 \text{ }^\circ\text{C}$, the thermal conductivity of carbon foam decreases to lower levels. On the other hand treatment up to higher temperatures results with graphitic structure that increases the thermal conductivity. It has been reported that carbon foam conducts heat six times higher than copper and four times higher than aluminum [18].

The properties of three different carbon foam produced at Oak Ridge National Laboratory (ORNL) and Aluminum are presented in Table 2.1.

Table 2.1 Oak Ridge National Laboratory (ORNL) carbon foam experimental properties and properties of aluminum [19]

ORNL Graphite Foam Experimental Properties					
	ORNL Foam I	ORNL Foam II	ORNL Foam III	Aluminum 6061	
Physical Properties					
Density	0.57	0.59	0.70	2.88	g/cm ³
Porosity	0.75	0.74	0.69	0	
Fraction Open Porosity	0.98	0.98	Not measured	0	
Average Cell Size	350	60	350-400	--	μm
Mechanical Properties					
Compressive Strength	2.1	5.0	5.1	--	MPa
Compressive Modulus	0.144	0.180	0.413	70	GPa
Thermal Properties					
Bulk Specific Thermal Conductivity	218	313	250	63	(W/m·K)/(g/cm ³)
Bulk Thermal Diffusivity	4.53	3.1	3.52	0.81	cm ² /s

A new generation of carbon foams began in the 90's as research focused on the production of carbon foams from alternative precursors such as pitches and coal. Typical processes utilize a blowing technique to produce carbon foam from the pitch precursor in which the pitch is melted and passed from a high-pressure region to a low-pressure region. Thermodynamically, this produces a "Flash" thereby causing the low molecular weight compounds in the pitch to vaporize (the pitch boils), resulting in a pitch foam. Then, the pitch foam must be oxidatively stabilized by heating in air (or oxygen) for many hours, thereby, cross-linking the structure and

"setting" the pitch so it does not melt during carbonization [14, 20]. This is a time-consuming step (up to 100 hours) and can be an expensive step depending on the particle size and equipment required. Without this oxidative stabilization step, the pitch may melt during further heat treatment [16, 20].

The "set" or oxidized pitch is then carbonized in an inert atmosphere to temperatures as high as 1100°C. Then, graphitization is performed at temperatures as high as 3000°C to produce a high thermal conductivity graphitic structure, resulting in stiff and very thermally conductive foam.

2.3. Mesophase Pitch Based Carbon Foam

Mesophase pitch based carbon foam was developed at the Wright Patterson Air Force Base Materials Lab in 1990's and it is recognized as an important industrial material [21]. A material suitable for foaming is Mitsubishi AR pitch. This is a synthetic naphthalene derived pitch, which is 100% anisotropic mesophase [14]. AR pitch is prepared by the catalytic polymerization of naphthalene using HF-BF₃ catalyst [22].

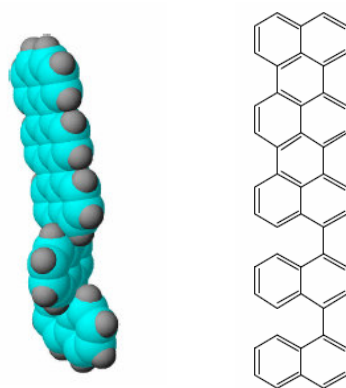


Figure 2.7: AR mesophase pitch [23].

Brooks and Taylor first discovered mesophase pitch in 1965. The term "mesophase" is used for the substance of which the spheres and the mosaic – before solidification – are formed [24]. Anisotropic mesophase is the intermediate product, which occurs during thermal pyrolysis of certain aromatic hydrocarbons.

Suitable mesophase pitch precursors include petroleum, coal tar or synthetic precursors [25]. Mesophase pitches derived from synthetic precursors, such as Mitsubishi AR pitch has more homogeneous compositions of the including molecules than mesophase pitch derived from coal tar or petroleum pitch [26]. Figure

2.7 shows us the schematically presentation of the structure of Mitsubishi AR mesophase pitch.

As the hydrocarbon is heat treated under inert gas atmosphere, it condenses to large, planar molecules, usually with evolution of hydrogen. These molecules may have a molecular weight of 500-1000 amu. As the molecules grow, they nucleate and grow a liquid crystal phase, called the mesophase. The liquid crystal phase can be thought of as the stacking of planar molecules, as an intermediate step in forming graphitic platelets. A 100% mesophase material would consist entirely of this liquid crystal material [25].

Figure 2.8 shows a simplified bloc and process flow diagram of the naphthalene derived mesophase pitch.

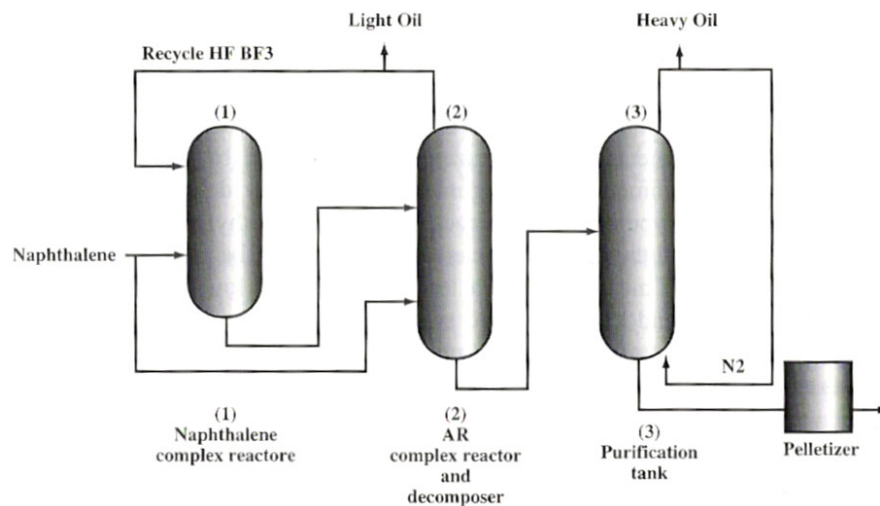
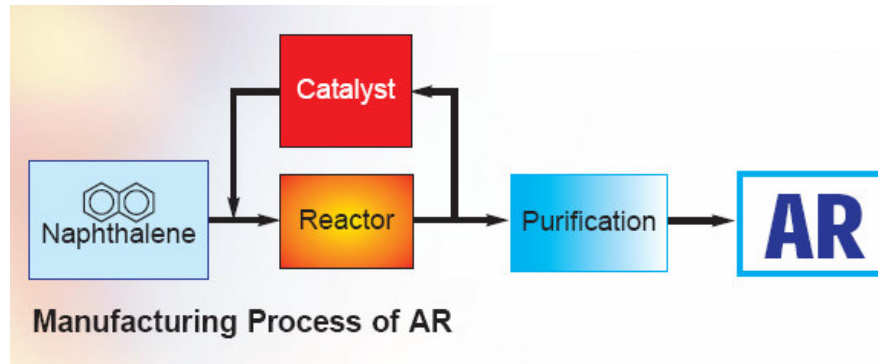


Figure 2.8: Block and process flow diagram of the naphthalene derived mesophase pitch [27].

The thermotropic nature of the synthetic mesophase pitch that means typically graphitizable [28] was obvious; the pitch fused into a liquid, whose viscosity decreased with increasing temperature while anisotropy, stacking of molecules and alignment of aromatic planes along the magnetic field were maintained. These facts suggest the more-ordered assembly of mesophase molecules in the liquid state [26].

Naphthalene and HF and BF_3 are mixed in a stirred tank reactor to form the naphthalene HF- BF_3 complex. The AR complex section is where the naphthalene complex is further reacted with naphthalene to form the AR/ HF- BF_3 in a stirred tank reactor. After the polymerization reaction, the AR/ HF-heating in the stirred tank reactor decomposes BF_3 . HF and BF_3 are recovered and recycled to the naphthalene complex section. At the same time, the light oil is recovered to assure 100 % anisotropy. The purification section is where nitrogen is blown into the purification tank to remove the low-boiling products, so adjusting the volatile contaminants in the AR resin. Solid contaminants are removed by filtration. Very pure AR resin melt is extruded into strands and cut into pellets [27].

Synthetic mesophase pitch is the preferred precursor for high thermal conductivity carbon materials because it is graphitizable. This implies that the internal structure of a carbon materials produced from mesophase pitch is similar to that of graphite. When a Synthetic mesophase pitch is used, the domains are stretched along the cell walls of the foam structure and thereby produce a highly aligned graphitic structure parallel to the cell walls [15].

The suitable solvents for mesophase pitch are THF (tetrahydrofuran), toluene, pyridine, benzene, and xylene. These are aromatic or conjugated compounds which are hydrogen donors. They will interact with and solubilize the mesophase pitch polyaromatic molecules and reduces to softening point of mesophase pitch [29].

Especially Kearns [20, 30], Murdie [28, 29, 31] and Klett [15, 16, 32] produced carbon foam using synthetic mesophase pitch as a precursor to produce carbon foam.

Process of carbon foam production from mesophase pitch is summarized briefly as follows; pitch is introduced into a mold, and the mold placed in a pressure vessel. It is heated from 10°C to 40°C above the melting temperature of the pitch. After, additional inert gas is introduced to obtain a pressure of about 68 atm., and waited under pressure for about 10 to 40 minutes. System is depressurized to atmospheric

pressure rapidly, thereby porous foam is provided. Then, it is stabilized at an elevated temperature in an air, finally carbonization and graphitization steps leads to obtain carbon foam.

All researchers approximately applied the same production method, although there are some differences such as Murdie solved mesophase pitch with solvent and removed it after pressure releasing [29], while Kearns applied initial pressure about 23-25 bars before heating the sample [30]. In addition Klett heated the sample about 500-600°C instead of 10 to 40°C above the melting temperature of the pitch [16].

2.4. Stabilization, Carbonization and Graphitization of Carbon Foam

2.4.1. Stabilization

Stabilization is important step to produce carbon foam clearly. When the carbon foam is made from a thermoplastic material such as a mesophase pitch, usually it is necessary to cross link the foam by oxidation before it can be heated to carbonization temperatures. Without this oxidation (stabilization) step, the pitch may melt during carbonization step. [16].

Convenient stabilization temperature is above the 10-60°C of melting temperature of pitch. If these temperatures are exceeded, the oxidized layer becomes too thick with a resultant deterioration in the properties of the carbon foams. If the temperature is too low, the rate of oxidation may be insufficient and the pores may have a tendency to close during the carbonization [14].

In general, stabilization can be carried out about 8 to 24 hours with an air or oxygen atmosphere until a weight gain of about 5 to 10% is achieved [30]. Heat up should be at a constant about 1°C/minute to about 10°C/minute or stepwise [33]. The resulting, stabilized porous foam is cooled to ambient temperature at a cooling rate of about 0.1°C/minute to 5°C/minute, so as to prevent thermal stresses in the foam [30].

2.4.2. Carbonization

Carbonization is a simply heating cycle. Many researchers are used various process conditions during the carbonization step. Some example of the process is given below: The precursor is heated slowly to a range of temperature, which depends on the nature of precursor and may be as high as 1300°C. The organic material is

decomposed in organic residue and volatile compounds diffuse out. The process is complex and several reactions may take place at the same time such as dehydrogenation, condensation and isomeration [34].

The stabilized porous foam can be carbonized by gradually heating the foam under an inert atmosphere to a temperature of about 800°C to 900°C until the hydrogen and oxygen in the molecular structure has been driven off [30]. Inert gases such as nitrogen, helium or argon may be used, preferably in the form of a stream of gas. It is important to accurately control the rise in temperature, to avoid thermal stresses, which could cause cracks in the foam. Accordingly, the heating rate should be about 1°C/minute to 5°C/minute. The resulting porous carbon foam should be held at the final temperature for at least 1 hour and the cooled down slowly, for example at about 5°C/minute to room temperature [34].

2.4.3 Graphitization

Graphitization can be explained as the conversion to a well-ordered graphitic structure. This takes place during heat treatment at temperatures more than 2500°C. Additionally, the electrical and thermal conductivities of the material increase with graphitization [34].

Carbon foams may be heated to a high temperature of about 2400°C to 3000°C, under an inert atmosphere, to graphitize the foam. During this further heating, the remaining small quantity of hydrogen in the foam is almost eliminated. The inert gas used during this treatment can be of the same type as that used for the carbonization process. Soak time of 1 to 10 minutes at final temperature is generally applied on the processes [30].

3. THE ELEMENT BORON

The name Boron comes from the Arabic *buraq*, "white." and *baurach* in Persian languages. The element with the symbol B, of which atomic number is 5, atomic weight is 10.81 and the melting point is $2190 \pm 20^{\circ}\text{C}$, is located at the top of the 3rd Group of the Periodic table.

						2 He
	5 B	6 C	7 N	8 O	9 F	10 Ne
	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr

Figure 3.1: The element Boron on Periodic Table [35].

It is found on earth in soil, rocks and water both in crystal and amorphous forms. The rank of amount of boron on earth is about 10 ppm. The boron that is found in the nature consists of the mixture of two stable isotopes having mass numbers 10 (19 %) and 11 (8.2 %). It is reported that the living organisms evolves in presence of this element.

The boron element was firstly obtained by Gay-Lussac, Jacques Thenard and Sir Humphry Davy in 1808, when boron oxide was heated with potassium. They produced metallic potassium by electrolysis, and then used it to reduce borates to impure boron. Much pure boron could be obtained by reacting the bromide or chloride forms with hydrogen via the tantalum fiber. Being a chemically non-metal element, the boron crystal has an inert behavior when comes together with water, air and hydro-chloric / hydro-fluoric acids under normal conditions. It only transfers into boric acid with high concentration of nitric acid at high temperatures. On the other hand, at high temperatures, reacts with pure oxygen to form boric oxide (B_2O_3), under the same conditions it forms Boron Nitride (BN) with nitrogen, also forms

industrial compounds such as Magnesium Boride (Mg_3B_2) and Titanium diboride (TiB_2) reacting with some metals.

Boron does not occur naturally in elemental form. Even though the element boron takes place on earth at different ratios within more than 150 minerals in B_2O_3 form, economically boron minerals exist as hydrate compounds of calcium, sodium and magnesium elements. Boron minerals become ready to be used by related industries following the crushing, sieving, washing and grinding operations after the minerals are taken out of the mine [36].

Boron is one of the simplest of atoms. The only simpler ones are hydrogen, helium, lithium and beryllium. Boron occurs naturally as 80% B^{11} and 20% B^{10} .

Boron is found in a variety of similar minerals all related to *borax*, sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. The boron minerals which are commercially important are sodium borate, boric acid, borax, sodium tetraborate pentahydrate, kernite and etc.

Boron is a relatively rare element in the earth's crust, representing only 0.001%. Borax is found in large amounts in USA, Turkey, and South America. The natural deposits are dried-up lake beds. Molten borax reacts with metal oxides to form borates that dissolve in the melt, so it is a useful as a welding and soldering flux, and in colored enamels for iron.

The electron configuration of boron is $1s^2 2s^2 2p$. It has only three electrons to work with, so the ion is unpolarizable, and does not hydrate. For this reason, boron is not eager to donate electrons in an electrovalent bond, and can also not accept them easily. Therefore, most of its bonds are covalent, and even forms *half-bonds* in which only one electron is shared covalently, not the usual two. This gives boron an apparent valence of +6 that we shall see in some interesting compounds. The first ionization potential is 8.30 V, which is not unusually high.

The other commonly-used boron compounds are orthoboric acid, or simply boric or boracic acid, H_3BO_3 , and boron trioxide, B_2O_3 , its anhydride. Note that the formula for boric acid can be written $\text{B}(\text{OH})_3$, as boron hydroxide. If boron were a normal metal, the hydroxyl ions would separate in water, creating the trivalent boron ion B^{+++} . This, however, does not happen to the smallest degree, and boron does not form ionic bonds. Moreover, boric acid is not gelatinous like aluminum hydroxide,

but crystallizes nicely. Boron trifluoride, BF_3 is not an ionic compound like NaF , which has no ions in its crystals. Instead, the hydrogen atoms are lost long before the oxygen atoms.

Ordinary boron is a brown-black amorphous powder. Pure boron can be made as extremely hard yellow monoclinic crystals that are a semiconductor resembling silicon. Crystalline boron is an insulator at low temperatures, but becomes a conductor at elevated temperatures, as would be expected as carriers are thermally excited into the conduction band. Fabrication difficulties have so far prevented the use of boron as a semiconductor. The density of crystalline boron is 2.34 g/cc, of amorphous boron, 2.37. It melts at 2300°C and boils at 2550°C (some sources say 2040°C and 4100°C), so it is a very refractory substance. Boron fibers have been used in composite materials because of their great strength.

Boron is also used in borosilicate glasses, which are 12%-15% B_2O_3 , 80% SiO_2 , and 2% Al_2O_3 . Sodium, potassium, magnesium and calcium oxides are kept to minimal amounts, since it is their exclusion that gives the glass its desirable properties. "Pyrex" is a common trade name for a borosilicate glass. This glass is chemically resistant, and has a small coefficient of thermal expansion. Boron carbide, B_4C , harder than SiC , is formed by decomposing B_2O_3 with carbon in the electric furnace: $2\text{B}_2\text{O}_3 + 7\text{C} \rightarrow \text{B}_4\text{C} + 6\text{CO}$. It was first suggested for commercial use in 1934, and is an excellent abrasive. Boron nitride, BN , is another very hard compound, used in cutting tools. Boron nitride has remarkable properties and can be used to make a material as hard as diamond. The nitride also behaves like an electrical insulator but conducts heat like a metal [37]. There are numerous other borides with complex structures. Boron is also used in porcelain enamels for iron, and for tiles and sanitary ware.

Borax is necessary in small amounts for plant growth, one of the 16 essential nutrients. In larger amounts it is poisonous to plants, and the range can be small. For peaches, 1 ppm is required, but more than 5 ppm is toxic. If the signs of boron deficiency are noted in plants, a boron supplement can be applied. Borates can be used as non-toxic and non-specific herbicides. Borates are non-toxic to animals. Borates are more toxic to insects than to mammals. The boranes and similar gaseous compounds are quite poisonous. As usual, it is not an element that is intrinsically poisonous, but toxicity depends on structure [38].

Boron also has lubricating properties similar to graphite. The hydrides are easily oxidized with considerable energy liberation, and have been studied for use as rocket fuels. Demand is increasing for boron filaments, a high-strength, lightweight material chiefly employed for advanced aerospace structures [39].

Boron is similar to carbon in that it has a capacity to form stable covalently bonded molecular networks. Carbonates, metalboranes, phosphacboranes, and other families comprise thousands of compounds [39].

3.1. Boron Nitride

Boron nitride is a binary chemical compound, consisting of equal proportions of boron and nitrogen. It is a synthetic compound. Boron nitride is isoelectronic to the elemental forms of carbon and isomorphism occurs between the two species. That is boron nitride possess three polymorphic forms; one analogous to diamond, one analogous to graphite and ones analogous to the fullerenes. The diamond-like allotrope of boron nitride, known as Borazon, is one of the hardest materials known but is softer than materials such as diamond, ultra-hard fullerite, and aggregated diamond nanorods.

Boron nitride was first prepared in 1842 by reacting molten boric acid with potassium cyanide. In the 1950s, commercial production was initiated by Union Carbide and Carborundum Co. BN is a ceramic material with outstanding chemical, thermal and electrical properties. It can be used as a high-temperature solid lubricant, is stable at high temperatures and is not wetted by many metallic melts, such as aluminium and magnesium. BN shows good thermal shock resistance, high thermal conductivity and low dielectric constant.

Application areas of boron nitride can be listed as follows:

1. Chemical and metalurgy industries
2. High temperature technology
3. Electronic and electrotechnic
4. Refractor material
5. Cutting material for hard metals

6. Neutron absorbant in nuclear industry
7. All places where diamond is used, because it has a similar strength.

3.1.1. Forms of Boron Nitride

There are three different forms of boron nitride; hexagonal boron nitride (α -BN), cubic boron nitride (β -BN) and pyrolytic boron nitride (γ -BN) which is produced by chemical vapor reduction. Hexagonal boron nitride is the most commonly produced boron nitride, and cubic boron nitride comes after this. The third form of boron nitride is produced only for special cases.

Cubic boron nitride has very similar properties to diamond. This diamond-like allotrope of boron nitride is widely used as an abrasive for industrial tools. Such usefulness is derived from the insolubility of boron nitride in iron, nickel and related alloys at high temperatures (unlike diamond). Like diamond, it has good thermal conductivity, caused by phonons; this is a difference against metals, where the mediators are electrons. In contact with oxygen at high temperatures, BN forms a passivation layer of boron oxide. In Figure 3.2. A photograph of cubic boron nitride crystals can be seen.

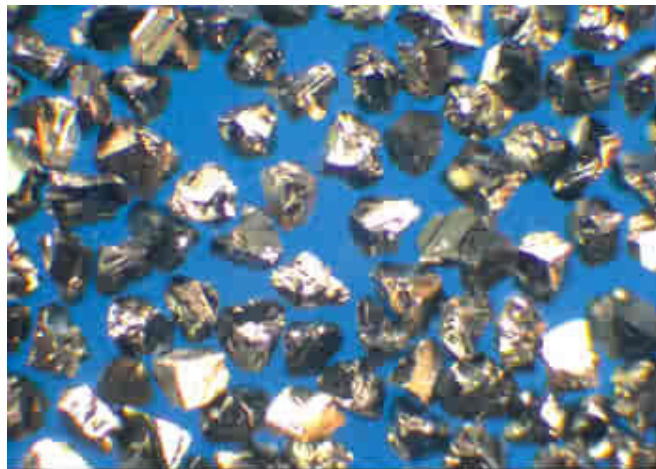


Figure 3.2: Photograph of cubic boron nitride [40].

Boron nitride binds well with metals, due to formation of interlayers of metal borides or nitrides. Materials with cubic boron nitride crystals are often used in the tool bits of cutting tools. Ceramic binders can be used as well.

Hexagonal boron nitride is a substance having unique properties such as high refractoriness and lubricity, low thermal expansion, high thermal conductivity, electrical isolation, chemical inertness and easy workability. Cubic boron nitride is the second hardest substance known after diamond. Due to its excellent thermal conductivity, it is used for cutting hard materials at high temperatures.

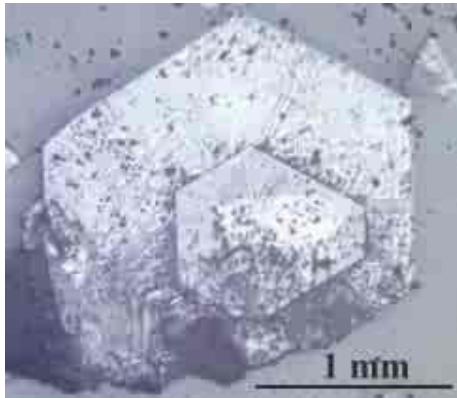


Figure 3.3: Photograph of hexagonal boron nitride [41].

Hexagonal Boron Nitride, also known as "White Graphite", is a ceramic material with excellent machinability. The "white graphite" provides the optimum material solution for a wide range of industrial applications, including those requiring electrically insulating properties, combined with thermal conductivity, as well as high temperature and oxidation resistance. The excellent release properties, coupled with the high resistance to wetting in applications involving molten metals and glass present many ground breaking opportunities for the application of this material [41].

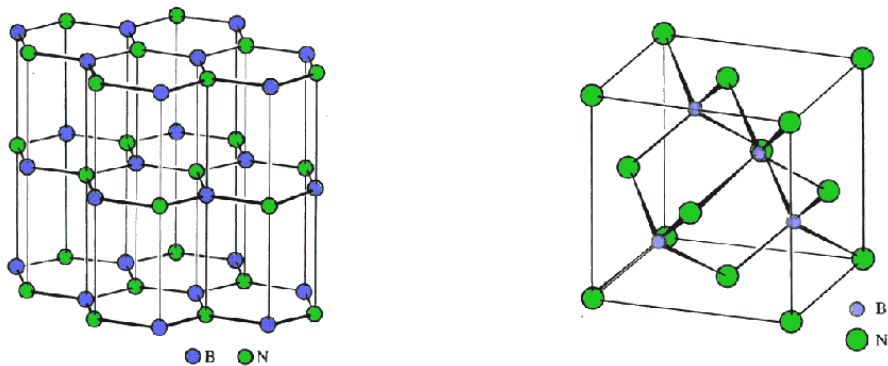
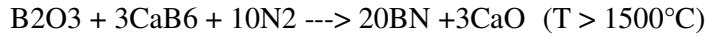
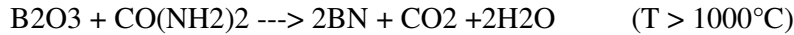
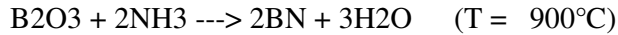


Figure 3.4: Schematic lattice of (a) Hexagonal boron nitride (b) Cubic boron nitride [42, 43].

3.1.2. Production of Boron Nitride

Three general reactions are used for the synthesis of α -BN:



These processes yield refractory grades with concentrations of 92%-95% BN and 5%-7% B₂O₃. The glassy B₂O₃ cannot be converted to BN. The B₂O₃ is removed by evaporation in a second step by reheating the product to temperatures >1500°C. The remaining ceramic-grade product has BN concentrations >98.5%.

Table 3. 1 The properties of boron nitride compared with other high temperature materials [42].

Properties	BN	ALUMINA	TECHNICAL GRAPHITE
Density	2,15-2,20	3,7-3,9	1,66 ± %10
Hardness	Mohs 2	Mohs 9	-
Melting Point	>3000 °C in N ₂ 2730 °C	2015 °C	3700 ± 100 °C
Electrical resistance Ohm-cm	1,7*10 ¹³ (at 25 °C) 3,1*10 ⁴ (at1000°C)	1*10 ¹⁶ (at 14 °C) 3*10 ¹³ (at 300 °C)	109*10 ⁻⁶ (at 25 °C) 8-15*10 ⁴ (at 1000 °C)
Diaelectric coefficient	4,15	9,0-10,0	-
Thermal expansion coefficient (cm/cm °C* 10 ⁻⁶)	0,7(⊥) 7,5 (//)	6-10	32(⊥) 46(//)
Working Temp(°C)			
Air media	1000	1600-1700	330
Nitrogen media	3000	2000	1650
Chlorine media	700	-	-
Thermal conductivity Watt/m °C	36 (//) 34 (⊥)	17-30	138(//) 95(⊥)

Hexagonal boron nitride (α -BN) is often called white graphite, because it has a graphite-like hexagonal layer structure, crystal form, smoothness and softness. In

contrast to graphite, however, BN is white and has a high electrical resistance. The reason for these differences, is the absence of the delocalized α -bonds in the BN structure. It has the lowest density (2.27 g/cm³) compared to all ceramic materials. In addition to its resistance to very high temperatures, it has a high thermal shock resistance (between 0-2000oC thermal shocks) [9-11]. Some physical, chemical and electrical properties of hexagonal boron nitride are compared with technical graphite and alumina in Table 3.1.

3.2. Boron Carbide

Boron Carbide is one of the hardest materials known, with a hardness of 9.3 on the Mohs scale, ranking third behind diamond and cubic boron nitride. It is the hardest material produced in tonnage quantities. Originally discovered in mid 19th century as a by-product in the production of metal borides, boron carbide was only studied in detail since 1930 [45].

Boron carbide powder is mainly produced by reacting carbon with B₂O₃ in an electric arc furnace, through carbothermal reduction or by gas phase reactions. For commercial use B₄C powders usually need to be milled and purified to remove metallic impurities.

As an alternative, B₄C can be formed as a coating on a suitable substrate by vapour phase reaction techniques e.g. using boron halides or di-borane with methane or another chemical carbon source.

Boron carbide is characterised by its:

- Extreme hardness
- Difficult to sinter to high relative densities without the use of sintering aids
- Good chemical resistance
- Good nuclear properties
- Low density

Boron carbide is an extremely hard ceramic material used in tank armor, bulletproof vests, and numerous industrial applications.

Its ability to absorb neutrons without forming long lived radio-nuclides make the material attractive as an absorbent for neutron radiation arising in nuclear power

plants. Nuclear applications of boron carbide include shielding, and control rod and shut down pellets.

Table 3.2. Properties of boron carbide [46].

Property	
Density (g.cm ⁻³)	2.52
Melting Point (°C)	2445
Hardness (Knoop 100g) (kg.mm ⁻²)	2900 – 3850
Fracture Toughness (MPa. m ^{-1/2})	2.9 – 3.7
Ypung's Modulus (GPa)	450 – 470
Electrical Conductivity (at 25°C) (S)	140
Thermal Conductivity (at 25°C) (W/m.K)	30 – 42
Thermal Expansion Co – eff. X 10 ⁻⁶ (°C)	5
Thermal neutron capture cross section (bam)	600

4. EXPERIMENTAL STUDY

4.1. Materials Used

4.1.1. Precursors

4.1.1.1. Mitsubishi AR Mesophase Pitch

The formation of optically anisotropic spheres in pitches (mesophase spheres) and their coalescence were demonstrated in 1964. In AFRL (U.S. Air Force Laboratory), which was set up as a full spectrum laboratory in 1997, the scientists were responsible for planning and executing the Air Force's entire science and technology. The researches developed the technology in their search for ways to exploit the extraordinary properties of aligned graphitic crystallites in carbon; the search was part of an investigation into new easy to manufacture composite reinforcements. The initial work led to a material called carbonaceous mesophase pitch, which is the precursor for most carbon fibers. The researches found that when the pitch is foamed to have an open-celled structure (75-95%), developed ligament like configurations containing the required aligned graphitic crystallites forms.

Mesophase pitch, meaning liquid crystal state pitch, is considered to be an important precursor for high performance carbon foams. In this study, naphthalene based synthetic mesophase pitch from Mitsubishi Gas Chemical Company Inc., which is labeled Mitsubishi AR, was used to produce carbon foam. The structure of mesophase pitch is given in Figure 4.1.

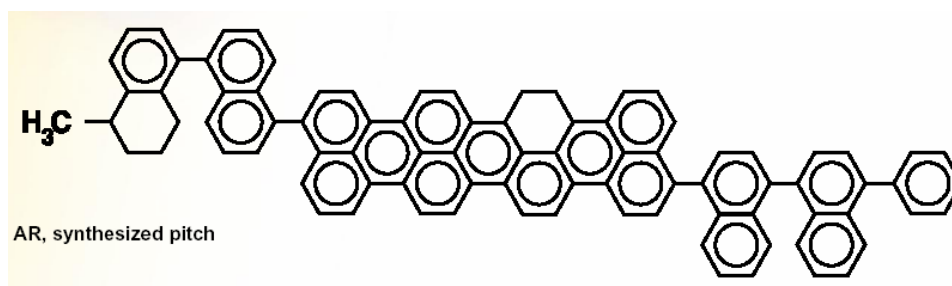


Figure 4.1: The chemical structure of Mitsubishi AR mesophase pitch [5]

The mesophase pitch is produced by catalytic reaction of naphthalene. The block flow diagram is shown in Figure 4. 2., and the properties of product are listed in Table 4.1.

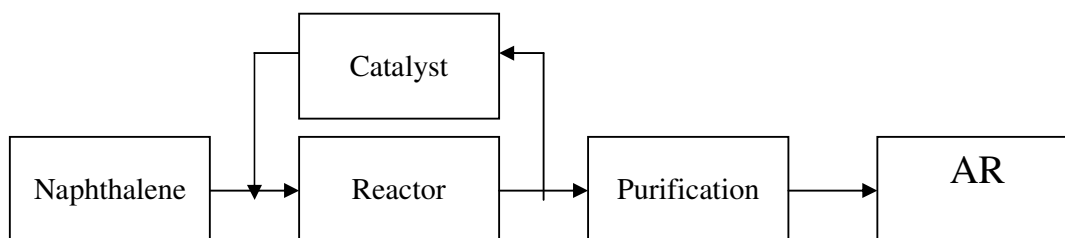


Figure 4.2: Manufacturing process of AR [6].

Table 4.1. Typical Properties of AR Pitch

Physical Properties	
Appearance	Black pellet (3mm*7mmL)
Bulk Density (g/cm ³)	>0.65
Specific Gravity (25°C)	1.23
Specific Heat (cal/g°C)	0.65
Softening Point (°C) by Mettler	275
Mesophase Content (%)	100
Hydrogen/Carbon (atom/atom)	0.58-0.64
Flash Point (°C)	>300
Ash(ppm)	<20
Melting Temperature (°C)	275-295
Solubility (%)	
Water soluble	0
Benzene soluble	35-44
Pyridine Insoluble	40-50

4.1.1.2. Different Mesophase Pitches

In this study three different mesophase pitches were used as precursors. The pitches are obtained from Mitsubishi Gas Company, Tokyo, Japan. The regular pitch; namely Mitsubishi AR mesophase pitch is produced by catalytic polymerization of naphthalene with the aid of HF-BF₃ catalyst. Naphthalene is aromatic hydrocarbon, so it is also called as a synthetic mesophase pitch. That pitch is the one used in the previous studies having a softening point value of 284°C. It is available in the form

of pellets. The other two pitches are 6T16 and EP050130. The softening points, availability and commercial status of these products can be seen on the Table 4.2.

Table 4.2. The pitches used in the experiments and their properties.

Code	Softening Point	Shape	Commercial Status
EP050130	251°C	Block	Laboratory sample
Ar251 (regular)	284°C	Pellet	Commercially available
6T16	295°C	Pellet	Not available anymore

4.1.2. Boron Nitride

Boron Nitride is obtained from the Faculty of Chemistry and Metallurgy, Metallurgical Engineering department of Istanbul Technical University. It is hexagonal boron nitride, which is produced in 95 % purity. The 5 % impurity is composed of boron oxide. Boron nitride has a density of 2.15 – 2.20 g/cm³. Boron nitride is mixed with hand to the mesophase pitch before the sample is put into the autoclave. Boron nitride is added to mesophase pitch in three different ratios; 0.1 %, 1 %, 10 %. The effects of these additions are investigated in this study.

4.1.3. Boron Carbide

Boron carbide is also obtained from Faculty of Chemistry and Metallurgy, Metallurgical Engineering department of Istanbul Technical University in this study. The density of the boron carbide sample is 2.52 g/cm³. Typical properties of boron carbide are exhibited on the Table 3.2 [46].

4.2. Experimental Procedure

Carbon foam process flow diagram is given in Figure 4. 2.

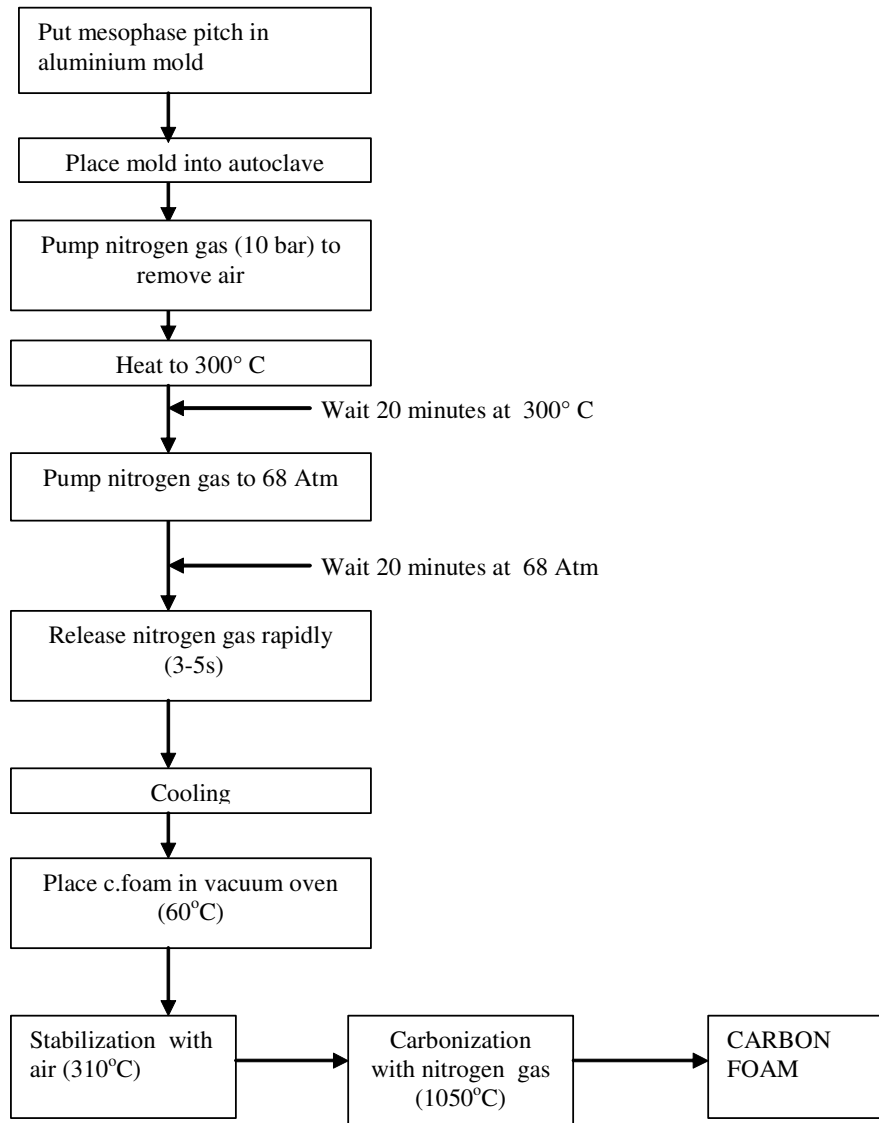


Figure 4.3: Process flow chart of the carbon foam [6].

4.2.1. Formation of Foam

The samples are prepared by using mesophase pitch. Boron nitride and boron carbide are mixed mechanically with the mesophase pitch. The samples that are produced with boron nitride and boron carbide are prepared by using the regular pitch, Ar241 which has the softening point value of 284°C. This is a different batch of the mesophase pitch used in the previous studies of Eksilioglu and Gencay [47, 48]. The compositions and production properties of the samples are shown in Table 4. 3.

Table 4.3. Compositions and production properties of the samples

Sample No.	Mesophase Pitch Used	Foaming Temperature	Additive	Percent of Additive	Softening Point of the Pitch
1	Ar251	300°C	-	-	284°C
2	Ar251	310°C	-	-	284°C
3	Ar251	320°C	-	-	284°C
4	EP050130	300°C	-	-	251°C
5	6T16	300°C	-	-	295°C
6	Ar251	300°C	BN	0.1 %	284°C
7	Ar251	300°C	BN	1 %	284°C
8	Ar251	300°C	BN	10 %	284°C
9	Ar251	300°C	B ₄ C	0.1 %	284°C
10	Ar251	300°C	B ₄ C	1 %	284°C
11	Ar251	300°C	B ₄ C	10 %	284°C

After characterization, the properties of the produced samples are compared with the properties of the regular pitch (Ar251) that is foamed at 300°C and have no additive which is shown on the first line of the Table 4.3.

Optimum foaming temperature was selected as 300°C in the previous studies of Eksilioglu who had produced foam at 280, 283, 293, 300°C [47].

Each sample is put into aluminum mold suitable for the desired final shape of the foam. Aluminum is chosen for the mold material because molten pitch doesn't wet aluminum, and thus, it will not stick to the mold [7].



Figure 4.4: The photograph of aluminum mold [47].

The mold is placed into a high-pressure autoclave. Autoclave is stainless steel (316SS) high temperature-high pressure cylinder vertical vessel with 5 cm diameter and 20 cm length. The photograph of the autoclave is shown in Figure 4.5.



Figure 4.5: The photograph of autoclave [47].

Before every experiment the air inside the system is purged out with nitrogen at 5-10 atmospheres pressure. Nitrogen vacuumed from the system after about 5 minutes soak time. This sweeping process is repeated at least two times to ensure the removal of air from the system. After sweeping is completed, the sample was heated. For the foams that are produced with regular Mitsubishi AR mesophase pitch the samples were produced at 300, 310 and 320°C, respectively. For the other precursors 300°C is chosen as the heating temperature, depending upon the previous studies.

The mesophase pitch is heated up to 300°C in 130 minutes with an acceleration rate of 2°C/min. The other samples that are produced at 310°C and 320°C are also kept heating at a rate of 2°C/min till they reach these temperatures. The heat-up trends of samples are illustrated in Figures 4.5 and 4.6. After reaching the target temperature, the autoclave is hold at this temperature for 20 minutes.

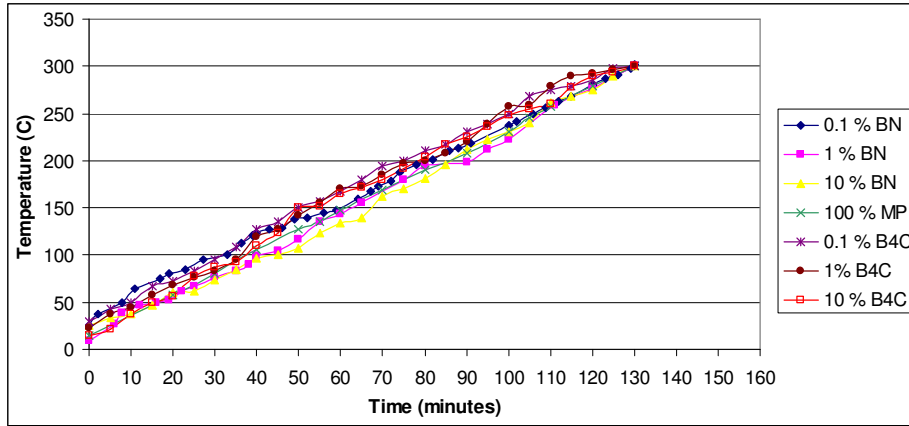


Figure 4.6: Autoclave Heat-up Trend for Foam formed with BN and B₄C additives.

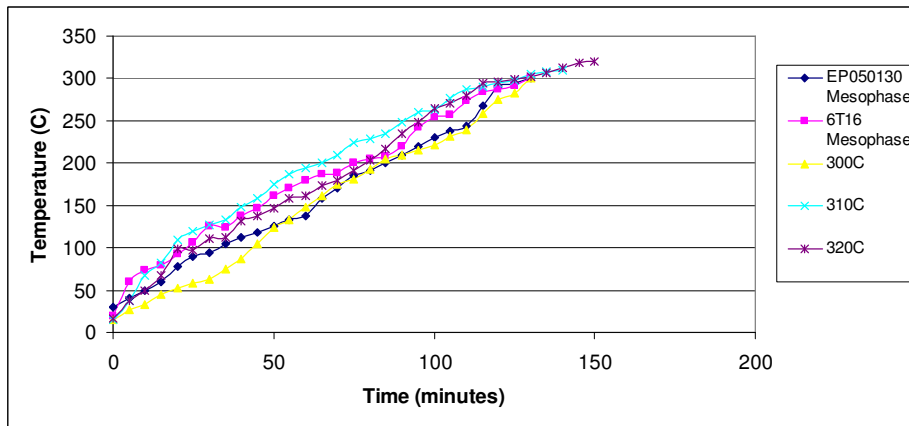


Figure 4.7: Autoclave Heat-up Trend for Foam formed at different temperatures and with different precursors.

Usually 15 minutes of soak time is applied at this temperature for homogeneous thermal stability. Later nitrogen is applied gradually to build up to pressure to the desired level (68 atm) in a 20 minutes period [48]. After reaching 68 bar, the autoclave is hold 20 minutes at this pressure.

Then, the pressure was released to the atmospheric pressure rapidly in 3-5 seconds, so that the porous foam can be obtained by the removal of the volatiles.

After all, the porous foam is let to cool to ambient temperature in the autoclave. Finally the foam is taken out and kept in a vacuum oven if is not subjected to stabilization immediately (Figure 4.7). Usually the foam is kept at 60°C in a vacuum oven in order to prevent any oxidation or other effects.



Figure 4.8: The photograph of vacuum oven [48].

4.2.2 Stabilization

Stabilization is the process, which makes the surface layer infusible so that the porous structure of the pitch foam is maintained in the subsequent heat treatments of carbonization and graphitization. When the carbon foam is made from a thermoplastic material such as a mesophase pitch, usually it is necessary to cross link the foam by oxidation before it can be heated to carbonization temperatures. Without this oxidation (stabilization) step, the pitch may melt during carbonization step [8].

Convenient stabilization temperature is above the 10-60°C of melting temperature of pitch. If these temperatures are exceeded, the oxidized layer becomes too thick with a resultant deterioration in the properties of the carbon foams. If the temperature is too

low, the rate of oxidation may be insufficient and the pores may have a tendency to close during the carbonization [9].

In this case, stabilization of the foams was carried out by subjecting the porous foam to an air atmosphere in a temperature-programmed furnace, which is shown below.



Figure 4.9: The temperature – programmed furnace where the stabilization and carbonization processes occur [48].

Preferably, a stream of gas is used, so that in addition to surface oxidation the products of the reaction are also removed. The rate of flow of oxidizing gas should be sufficient to give surface oxidation as well as removing volatile products. It may vary in the range of 50-200 l/hr... Preferably the oxidation temperature is increased gradually, and the rate of increase should be sufficiently slow to permit of a complete treatment [10]. In Table 4.4, thermal conditions used for stabilization process in this study are given.

Table 4.4 Stabilization Conditions Used in This Study [11].

Temperature (°C)	Acceleration rate (°C/min)	Holding time (min)
185	1.0	300
275	0.5	300
310	0.12	150
25	0.8	356.25

The resulting, stabilized porous foam is cooled to room temperature at a cooling rate of about 0.1-5.0°C/min [12]. In this study, cooling rate was taken as 0.8°C/min. to prevent thermal stresses in the foam. In order to examine the stabilized foam samples carbonization was not performed just after stabilization. It has been discovered that keeping the resulting foam 45 material warm, between 60-120°C until carbonization is important in order to prevent cracking of the foam material [13]. For this reason, the produced foams were again placed into the vacuum oven at 90°C.

4.2.3. Carbonization

The following step in the process is carbonization. The carbonization of the foams is carried out by gradual heating under an inert atmosphere to 1050°C. During the carbonization the hydrogen and oxygen in the molecular structure has been driven off, so that the carbonized product contains at least 98% carbon.

Non-oxidizing gases such as nitrogen, argon, hydrogen or helium may be used in the form of stream of gas, which removes the volatile products of the carbonization. The rate of flow of inert gas is reported to be between 5-150 l/h [14]. In this case, it was selected as 0.5 l/min. The inert gas used is nitrogen.

It is particularly important to control the rise in temperature, avoiding a rapid evolution of volatile products which could cause cracks in the foam. On the other hand, slow temperature rise produces orientation of the crystallites and increases the mechanical strength of the carbon foam [15].

The thermal conditions determined for carbonization process are shown in Table 4.5. The resulting carbon foam samples were cooled to room temperature at a cooling rate of about 0.8°C/min., so as to prevent thermal stresses in the foam. The thermal stress in the foam causes cracking and non-uniform structure [47].

Table 4. 5 Carbonization Conditions Used in This Study [16].

Temperature (°C)	Heating rate (°C/min)	Holding time (min)
310	1	60
750	0.5	60
1050	0.5	150
25	0.8	1281.25

4.3. Characterization

Characterization of produced carbon foam includes, scanning electron microscopy (SEM), density measurement, helium pycnometry, mercury porosimetry and compressive strength test.

4.3.1. Scanning Electron Microscope (SEM)

The technique of electron microscopy consists of bombardment of a sample surface with primary electrons that leads to the formation of secondary and backscattered electrons on the sample. These electrons are then detected and converted into images by the secondary electron (SE) and backscattered electron (BSE) detectors. In this study, Scanning Electron Microscope studies are carried out on JEOL JSM-840 Scanning Electron Microscope (SEM) [17].

Scanning electron microscopy (SEM) has been commonly used to observe the morphology of the materials, including carbon materials. The raster movement is accomplished by means of small coils of wire carrying the controlling current (the scan coils). Rastering the beam on the surface provides an elemental map of the surface [18].

In materials that consist of an element with a low atomic number, such as C, the electron beam can penetrate and so the SEM images obtained are the accumulation of secondary electrons reflected from all parts along the depth of penetration. As a consequence, the image is not obtained from the exact surface of the carbon material. Therefore, using a low acceleration voltage for the electron beam is preferred. In this study 5 – 10 KV of acceleration voltage is applied [19].



Figure 4.10: A view of a scanning electron microscope with secondary electrons forming the images on the TV screen [20].

4.3.2 Density

Density, or as it is known bulk density, is obtained by measuring the volume and mass of samples. To calculate volumes, the samples are shaped like rectangular prism, and all sides are measured. After all, the rectangular shaped samples are weighed. In order to reach the density measurements m/V ratio is used.

4.3.3 Mercury Porosimetry

Mercury porosimetry is widely used to characterize the pore structure of carbon foam. It is a relatively rapid method, which determines a wide pore diameter range ($0.003\mu\text{m}$ – $360\mu\text{m}$) and variety of porosity parameters. In mercury porosimetry, gas is evacuated from the sample cell, and mercury is then transferred into the sample cell under vacuum and pressure is applied to force mercury into the sample. Porosity analysis of the carbon foam samples was performed on Micromeritics Autopore 9220 Mercury porosimeter. A general view of the porosimetry equipment is shown in Figure 4.10. During measurement, applied pressure P and intruded volume of mercury, V , are registered. As a result of analysis, an intrusion-extrusion curve is obtained. The data produced can be used to calculate numerous sample characteristics such as pore size distributions, total pore volume, total pore surface area, median pore diameter, and sample densities (bulk and skeletal).



Figure 4.11: Mercury porosimetry equipment [48]

On the basis of the skeleton density and the bulk density, the total pore volume of a material can be calculated. The apparent density, also known as the mercury or bulk density is defined as the mass of a unit volume of the material including its pore system. The skeletal density, i.e. the structural or solid density, is determined with helium is defined as the mass of a unit volume of the solid, inaccessible to mercury.

Total porosity value is determined as follows where $\rho(s)$ is the skeletal density (g/m^3) and $\rho(b)$ is the bulk density (g/m^3) of the foam material [21]:

$$\% \text{ Porosity} = [1 - \rho(s) / \rho(b)] \times 100 \quad (4.1.)$$

4.3.4 Compressive Strength Test

Compression test is the method for determining behavior of materials under crushing loads. Specimen is compressed, and deformation at various loads is recorded. Compression strength is the maximum stress a material can sustain under crush loading and is calculated by dividing the maximum load by the original cross-sectional area of a specimen in a compression test.

In order to measure compression strength of the samples, Instron Model 1195 Tension/Compression tester is used. This equipment has ability to supply pressures up to 10 tones for compression of metals, paper, plastics, fabrics, wire of all gauges, rubber, or any other specialized materials [22].



Figure 4.12: Compression test equipment [48]

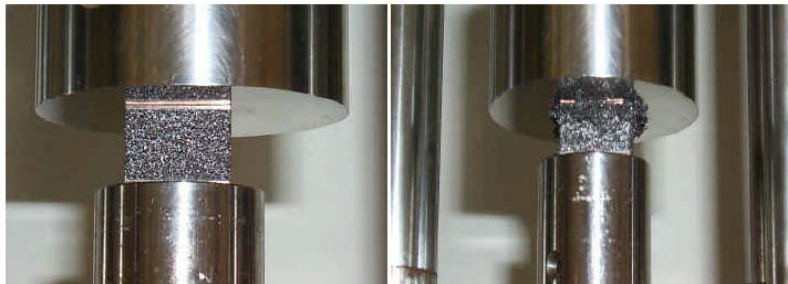


Figure 4.13: Carbon foam samples at compression test [48].

5. RESULTS AND DISCUSSION

The characteristic properties of the carbon foams produced are investigated with respect to the parameters involved such as temperature, additives and precursor by further using the characterization results.

Carbon foam produced was examined with scanning electron microscopy (SEM), mercury porosimetry, helium pycnometry, and compressive strength testing. The results of all experiments are presented below.

5.1. The Properties of the Carbon Foam Produced with the Mitsubishi AR Pitch at 300°C

In this study the whole group of carbon foams produced at different conditions with different properties such as BN and B₄C additive, softening point differences and foaming temperature are compared to the Mitsubishi AR sample that is produced at 300°C and 68 bar pressure with 5 seconds pressure release time.

Standard foam sample is prepared by using the regular pitch, which is used in the previous studies, namely Ar 251 precursor [47]. It is prepared by 100 % mesophase pitch which has a softening point of 284°C.

The SEM micrographs of the standard carbon foam produced are presented in Figure 5.1 (a) and (b). In order to interpret the foam quality it may be appropriate to consider the literature on foaming mechanism.

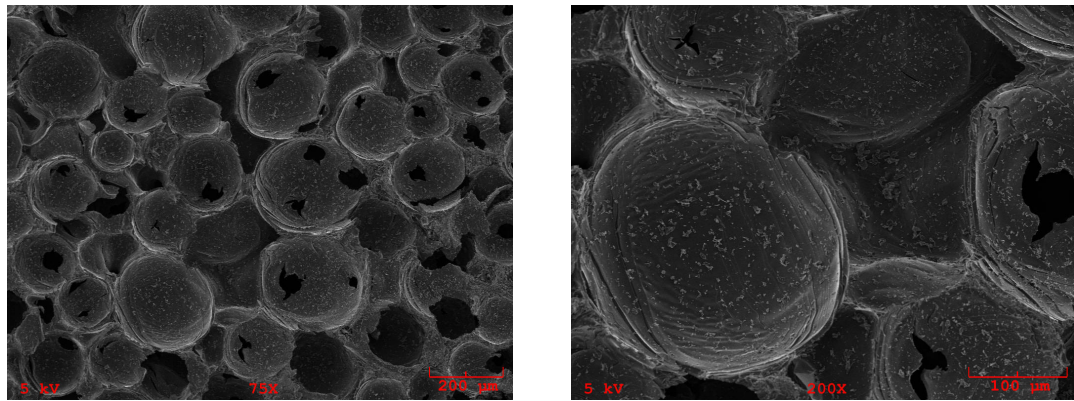
There are two descriptions for the microstructure formation of the carbon foams. The first one considers foaming as a result of the thermodynamic perturbation at the time of pressure release, bubbles form and expand in the molten precursor foaming the cellular nature of the subsequent foam [49]. In the second approach it is also explained that volatiles are formed under pressure which coalesce into bubbles to form cells and at the sudden pressure release operation flow of volatiles form pores preferentially open pores (Eksilioglu et. al.) [47]. The manner and extent to which these bubbles grow determine the foam's microstructure and hence the thermal,

electrical and mechanical properties of the final material. Thus, the properties are dependent on the precursor and micro structural arrangements [50]. Lo, asserted that equivalent modulus and Poisson ratio of the foam could be related to bulk material properties in an inverse linear relationship to the porosity.

As it can be observed from Figure 5.1; that the bubble sizes vary from location to location causing differences in thickness and elongation in the nodes and ligaments of the foam. However, under this irregular behaviour ligaments exhibit a preferential orientation.

High regions of graphitic order lead to foams having lower mechanical properties than that predicted.

Using a similar brand name mesophase pitch Eksioglu found a higher 0.56 g/cm^3 density compared to 0.45 g/cm^3 and porosity of 80.6% compared to 72.2% and a lower compressive strength of 3.3MPa compared to 2.12 compared to this study. Since experimental conditions are similar this difference may be attributed to the precursor which reported to have 1°C difference in softening points.



(a) at 300°C 75x (b) at 300°C 700x
Figure 5.1: SEM micrographs of carbon foam produced with 100 % Mitsubishi AR mesophase pitch at 300°C .

The other characterisation properties of this sample can be seen on the Table 5.1.

Table 5.1. Properties of carbon foam produced with 100 % Mesophase pitch at 300°C .

Density (Bulk)	Density (Solid)	Compressive Strength	Porosity
$0.4497 \text{ (g/cm}^3\text{)}$	$1.6178 \text{ (g/cm}^3\text{)}$	2.1235 (MPa)	72.2030 %

5.2. The Effect of Boron Nitride Additive on Carbon Foam Production

In this section the characterisation results of the carbon foam produced with boron nitride additive are examined. These samples are produced at 300°C, 68 bar pressure and with 5 seconds release time. As a precursor, Mitsubishi AR Pitch (Ar251) is used. Three different ratios of BN additive, 0.1 %, 1 % and 10 %, and also the carbon foam produced with 100 % mesophase pitch, are compared.

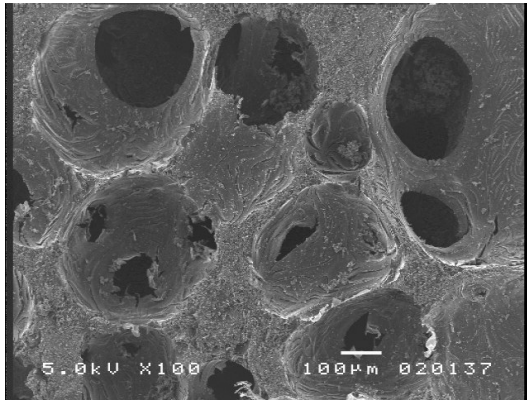
5.2.1. SEM Micrographs

The scanning electron microscopy photographs of the carbon foams produced with three different ratios of boron nitride additive; 0.1 %, 1 % and 10%; are given in Figure 5.2, 5.3 and 5.4, respectively. In the Figure 5.2, 5.3 and 5.4 a1, b1 ,c1 are the SEM micrographs taken at 75 magnification for the samples with 0.1 %, 1 % and 10% boron nitride additive respectively and a2, b2, c2 are the SEM micrographs taken at 200 magnification for the samples with 0.1 %, 1 % and 10% boron nitride additive respectively.

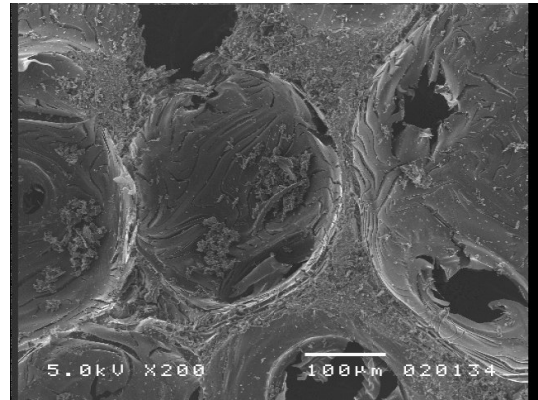
At 0.1 % BN addition the cell formation resembles closely to reference carbon foam obtained from 100% AR pitch processed at 300°C. However the cell geometry started to deteriorate, the pores started to chop in shape and numbers of them are changed. For the case of 1% BN the cell shape still seems to be similar to standard case but many irregular pores are formed.

For the case of 10% BN the pores coalesced into sizes comparable to cells and foam characteristics are not intact. Even though the cell geometry is well deteriorated the ligaments seems to be retained.

As can be seen from SEM images of carbon foams obtained with the addition of BN, the formation of pores seems to be increased. The pore sizes are also increased with the increasing amount of BN. Further addition of BN (10 %) diminishes the depth length of the cells.

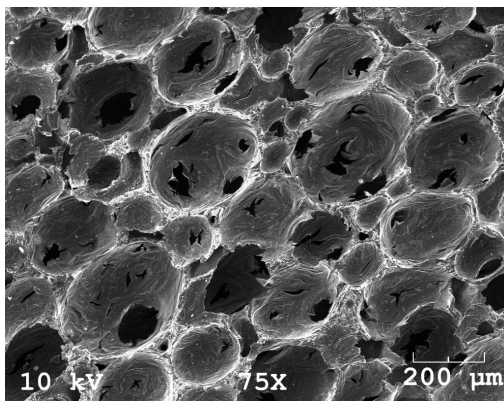


(a1) %0.1 BN 75x

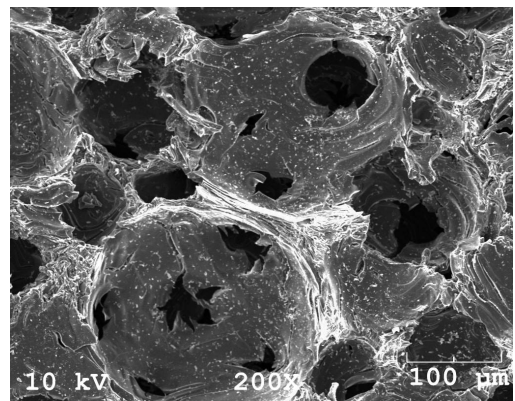


(a2) %0.1 BN 200x

Figure 5.2: SEM micrographs of carbon foam produced with 0.1 % BN additive.

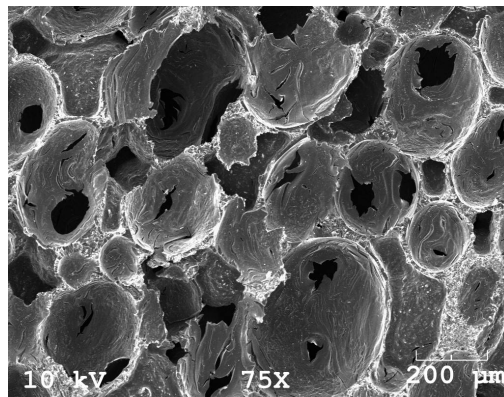


(b1) %1 BN 75x

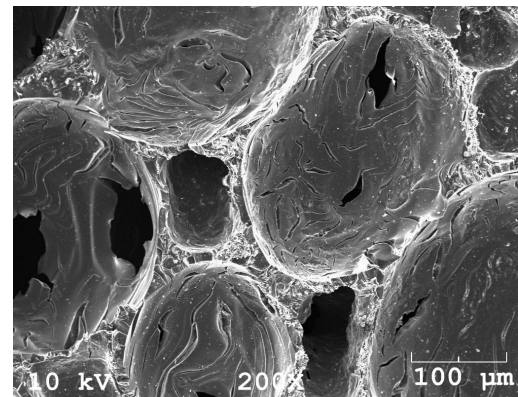


(b2) %1 BN 200x

Figure 5.3: SEM micrographs of carbon foam produced with 1 % BN additive.



(c1) %10 BN 75x



(c2) %10 BN 200x

Figure 5.4: SEM micrographs of carbon foam produced with 10 % BN additive.

5.2.2. Density Measurements Depending on the Mass / Volume Ratio

In Table 5.2, the average dimensions of each rectangular prism that are taken from the carbon foam samples that are clear-cut as much as possible with a ribbon saw.

By using the average side measures that can be seen at the Table 5.2 area and volume of the samples are calculated. The density is calculated by using these values, mass is divided by volume. Volume and density values of samples are presented in Table 5.4 below.

On the graph, in Figure 5.5, the change of density with increasing BN ratio is presented. So, it can be seen that the density of the carbon foam sharply decreases with the addition of BN. Further addition of BN the density increases slightly.

The sharp decrease in the density with BN addition may be interpreted as BN affecting the foaming mechanism to act against compaction mechanism which caused a reduction in density. This is in agreement with the increased number of pores in the cells which are also increased in size. The slight increase in the density at 10% BN addition is expected to be result of direct density of the additives reflecting on the foam density, the density of BN being 2.15 – 2.20 g/cm³.

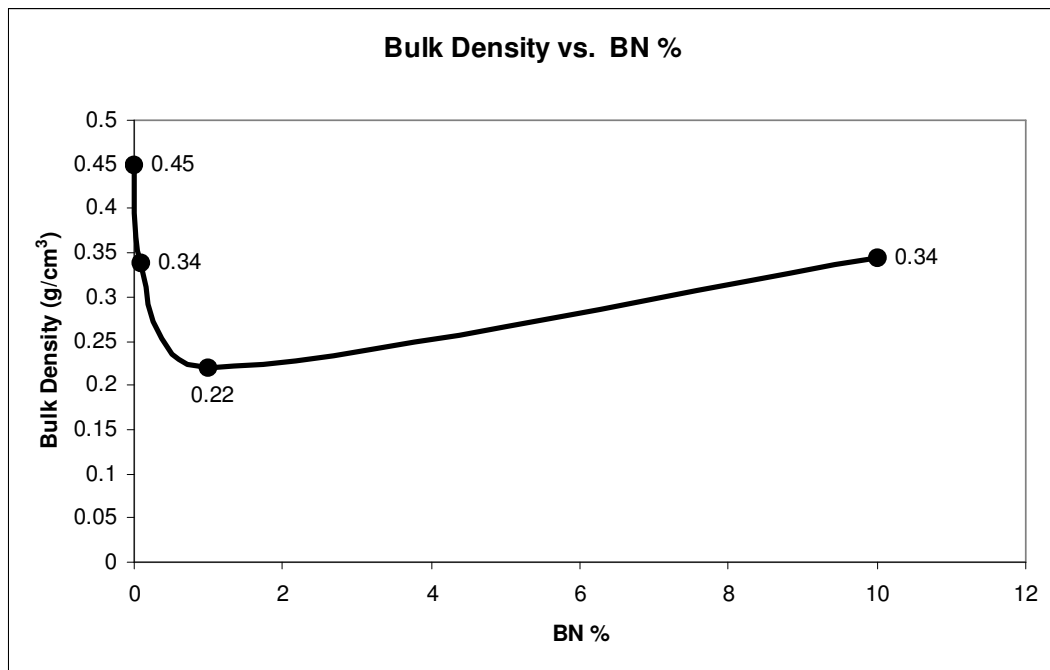


Figure 5.5: The graphic of the change in density of the carbon foam depending upon the percent of boron nitride additive.

5.2.3. Compressive Strength Analysis

In Figure 5.6, the change in the compressive strength of the carbon foams depending upon the BN ratio is presented.

The results presented in Figure 5.6 reflect the findings reported on density. The compressive strengths decreased in parallel to the decrease in density of the foams with increasing BN addition and increased at the highest level of BN addition like the case for density. It is not possible to give a full explanation why the compressive strength increased with 10% BN addition. This may be due to some complications in foaming mechanism with increasing BN content or it may be due to the contribution of BN to the foam structure.

Also, by looking at those two graphs, in Figure 5.5 and Figure 5.6, we can say that the density and compressive strength are related directly.

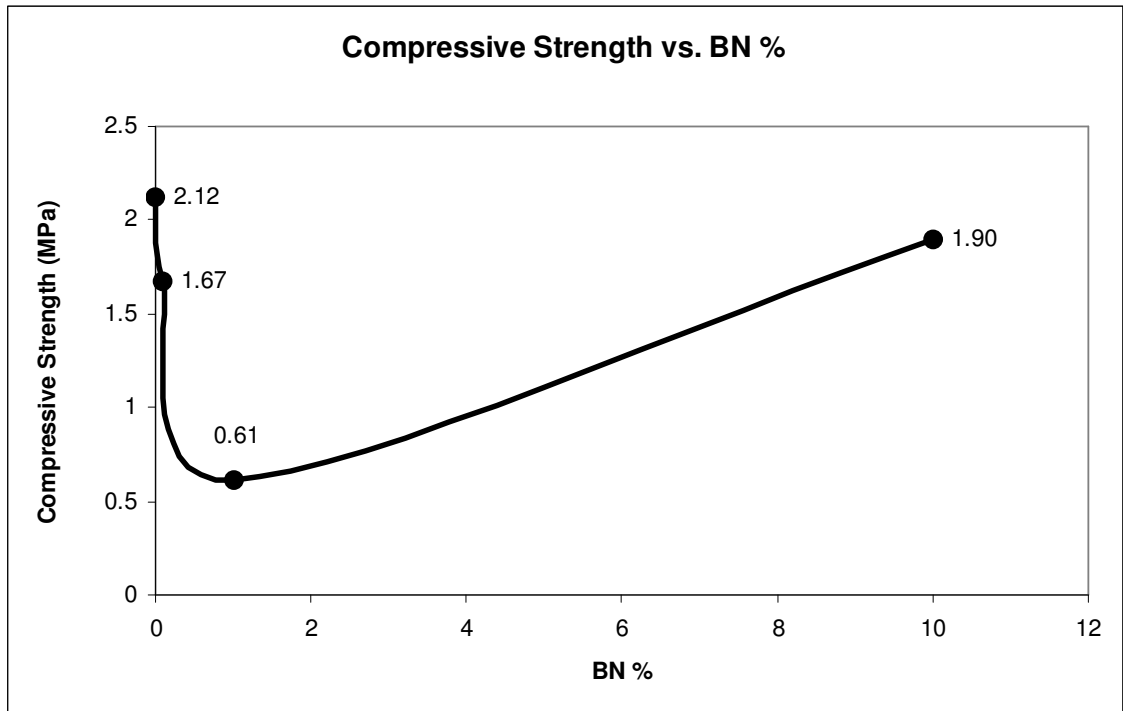


Figure 5.6: The graphic of the change in compressive strength of the carbon foam depending upon the percent of boron nitride additive.

5.3. The Effect of Boron Carbide Additive on Carbon Foam Production

Boron nitride was added to AR mesophase pitch mainly due to the reason that of the graphitization stage, the graphitic structure of inorganic BN and the graphitic structure of organic foam may work together. In order to make another possible chemical combination B_4C is used as additive in order to hope for C – C interaction between foam and boron carbide, since the composite characteristics of B_4C is well known.

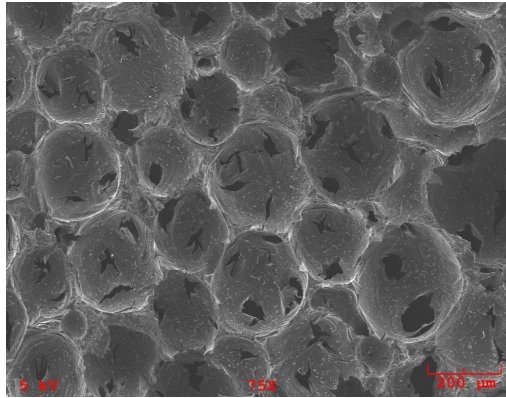
In this section the characterisation results of the carbon foam produced with boron carbide additive are examined. These samples are produced at $300^\circ C$ and 68 bar pressure and 5 seconds pressure release time. As a precursor, Mitsubishi AR Pitch (Ar251) is used. Three different ratios of B_4C additive, which are 0.1 %, 1 % and 10 %, and also the carbon foam produced without addition of B_4C , which is 100 % mesophase pitch, are compared.

5.3.1. SEM Micrographs

The scanning electron microscopy micrographs of the carbon foams produced with three different ratios of boron carbide additive; 0.1 %, 1 % and 10%; are given in Figures 5.7, 5.8 and 5.9, respectively. In the Figures 5.7, 5.8 and 5.9 a1, b1 ,c1 are the SEM micrographs taken at 75 magnification for the samples with 0.1 %, 1 % and 10% boron carbide additive respectively and a2, b2, c2 are the SEM micrographs taken at 200 magnification for the samples with 0.1 %, 1 % and 10% boron nitride additive respectively.

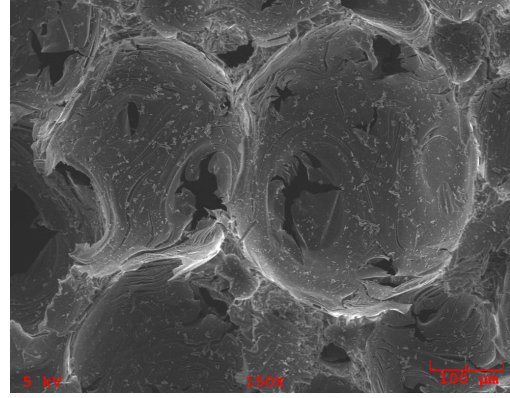
As seen in the micrographs the addition of B_4C disturbs the cell formation. The pore geometries are not circular. They look like scratches on the foam surface. The occurrence of narrow ligaments and cell formation are not observed as the amount of added B_4C is increased. The foaming is not uniform.

As observed from Figure 5.7 the cell and geometry of 0.1% B_4C addition affected slightly, but the effect on pore characteristics is more pronounced. The effect of 1% B_4C addition on pores is more drastic than 1% BN in which the structure is so thorn by the pores the cell geometries are affected considerably. For the case of 10% B_4C addition cells are more pronounced and the number of the pores is much less.



(a1) %0.1 B₄C

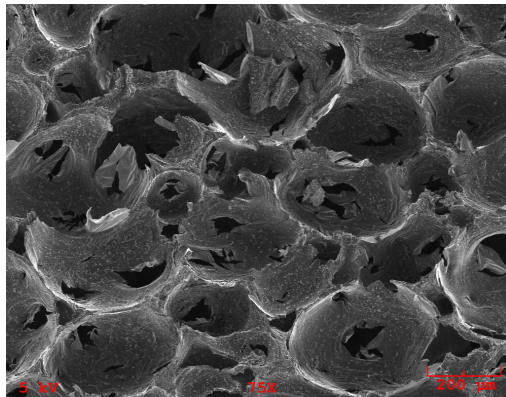
75x



(a2) %0.1 B₄C

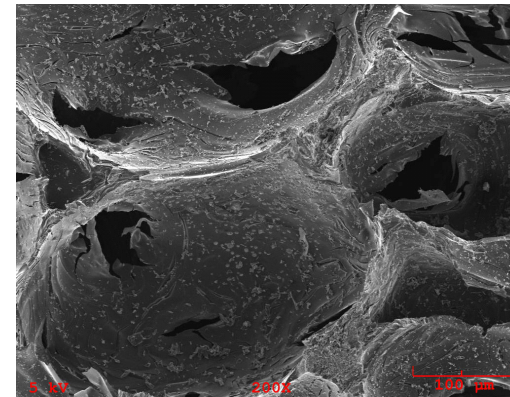
200x

Figure 5.7: SEM Micrographs of Carbon Foam Produced with 0.1 % B₄C Additive



(b1) %1 B₄C

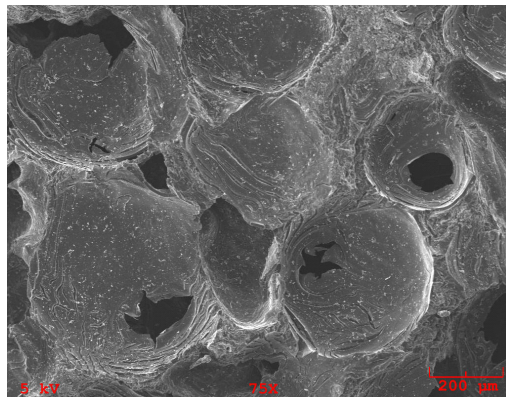
75x



(b2) %1 B₄C

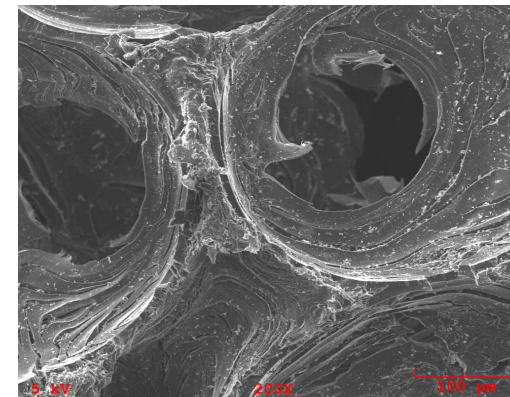
200x

Figure 5.8: SEM Micrographs of Carbon Foam Produced with 1 % B₄C Additive



(c1) %10 B₄C

75x



(c2) %10 B₄C

200x

Figure 5.9: SEM Micrographs of Carbon Foam Produced with 10 % B₄C Additive

5.3.2. Density Measurements Depending on the Mass / Volume Ratio

In this case, similar to the addition of BN, the addition of B₄C firstly decreases the density sharply. Further addition of B₄C causes the density to increase. This increasing tendency is clearer than that is in the Figure 5.5. From the similarity between the Figure 5.5 and , 5.10, we can say that there is an analogy between the two cases of BN and B₄C addition.

The densities of the carbon foams obtained by 0 %, 0.1 %, 1 %, 10 % B₄C are given in Figure 5.10. With the addition of B₄C the density at first decreased for 0.1 % and 1 % addition and increased for 10 % B₄C in a parallel movement with BN addition. This time the 10 % B₄C addition resulted in a higher density increase than 10 % BN addition. This is consistent with the fact that B₄C has a slightly higher density (2.52 g/cm³) than BN (2.15 – 2.20 g/cm³).

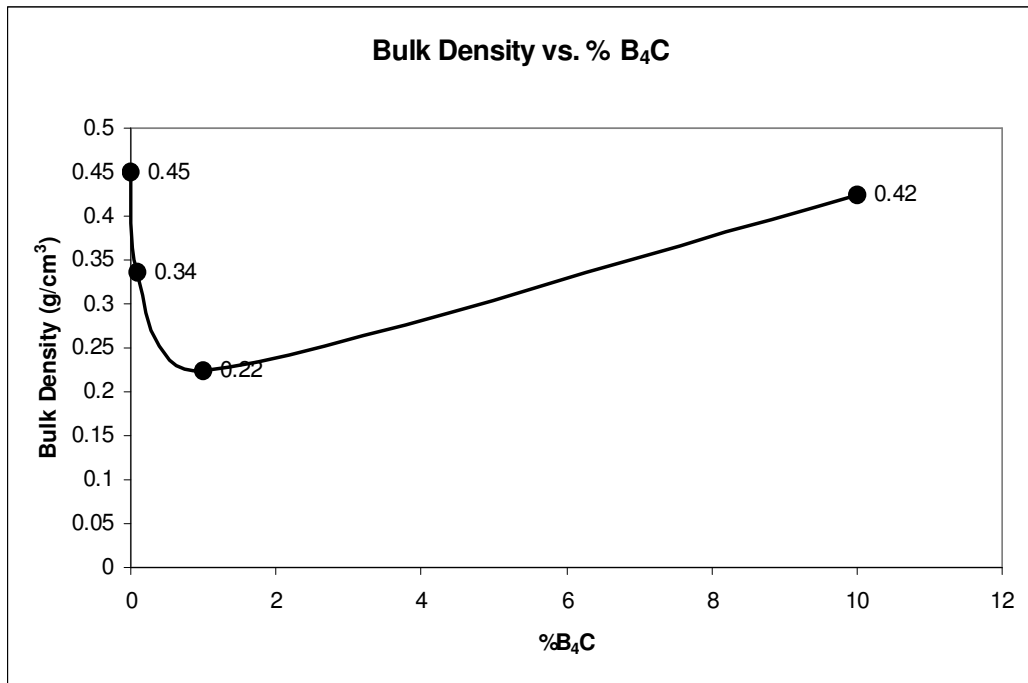


Figure 5.10: The graphic of the change in density of the carbon foam depending upon the percent of boron carbide additive.

5.3.3. Compressive Strength Analysis

Compressive strength test results of the samples are given in Figure 5.11.

As it is so for the density behaviours of the BN and B₄C addition to the foam, here in the Figure 5.11, it may be said that there is an analogy between the compressive strength behaviours of the carbon foams BN and B₄C added. It is also clear that the compressive strength and density behaviours have a similarity in these ceramic materials. The compressive strength of the B₄C added carbon foam seems to decrease sharply at first, and then in further addition the compressive strength slightly increases as if it is going to come to an equilibrium value.

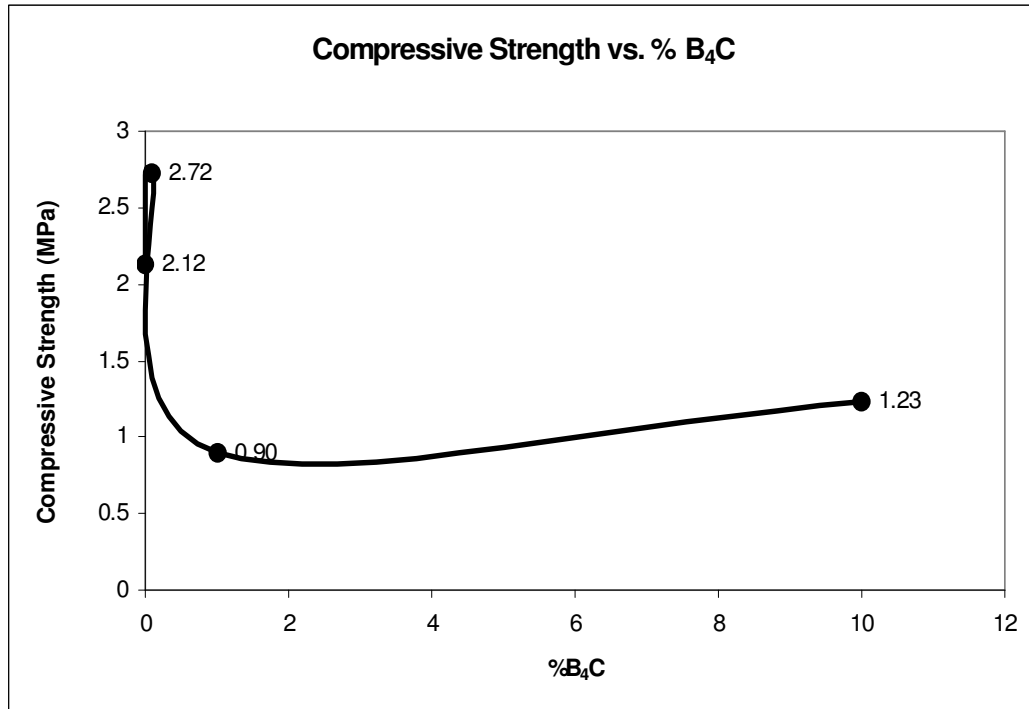


Figure 5.11: The graphic of the change in compressive strength of the carbon foam depending upon the percent of boron carbide additive.

5.4. The Effect of Foaming Temperature on Carbon Foam Production

In a previous study Eksilioglu carried out a carbon foam production studies from AR mesophase pitch using temperatures of 280, 283, 293, 300°C. In the study 300°C was found to be the optimum temperature. However, higher temperatures were not investigated due to the temperature limitation of the reactor. In this study higher temperatures; 310 and 320°C are also investigated to see the effect of temperature increase.

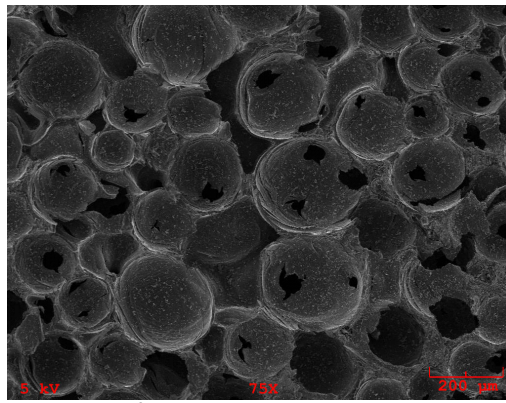
In this section the characterisation results of the carbon foam produced at 300°C, 310°C and 320°C are examined. These samples are produced with Mitsubishi AR Pitch (Ar251) as a precursor. All of the samples are produced at 68 bar pressure with 5 seconds release time.

5.4.1. SEM Micrographs

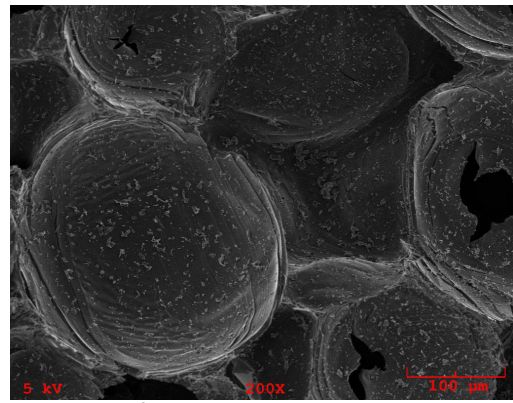
The scanning electron microscopy micrographs of the carbon foams produced at three different temperatures; 300°C, 310°C, 320°C; are given in Figures 5.12, 5.13 and 5.14, respectively. In the Figures 5.12, 5.13 and 5.14 a1, b1, c1 are the SEM micrographs taken at 75 magnification for the samples produced at 300°C, 310°C, 320°C respectively and a2, b2, c2 are the SEM micrographs taken at 200 magnification for the samples produced at 300°C, 310°C, 320°C respectively.

In the Figure 5.11, we can see that the cells are more circular and the boundaries are clearer for the sample that is produced at 300°C. The ligaments are also clear and regular. There are a few pores inside the cells and the sample contains non-porous cells.

The electro micrographs show that all the foams produced at 300, 310, 320°C have circular cell structures. The pores in the cells are showing some differences. The pores for the case of 300, 310 and 320°C foams show decreased irregularities as temperature is increased. Also with increased temperature the ligaments are also more developed. These differences are interpreted as a function of viscosity. As the temperatures are increased the viscosity is reduced to enable the pitch to let itself subject to stretching and pore formation becomes easier function.

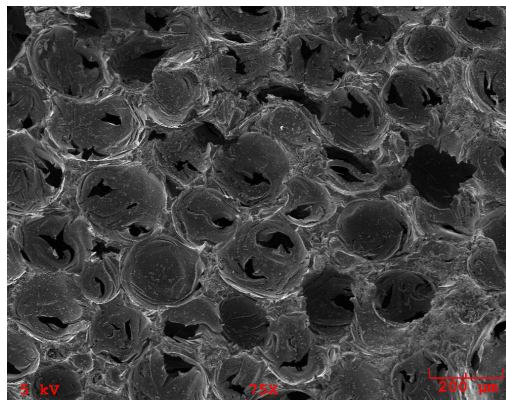


(a1) @300°C 75x

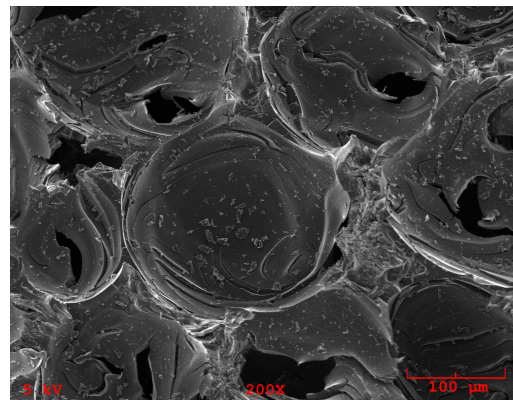


(a2) @300°C 200x

Figure 5.12: SEM Micrographs of Carbon Foam Produced at 300°C.

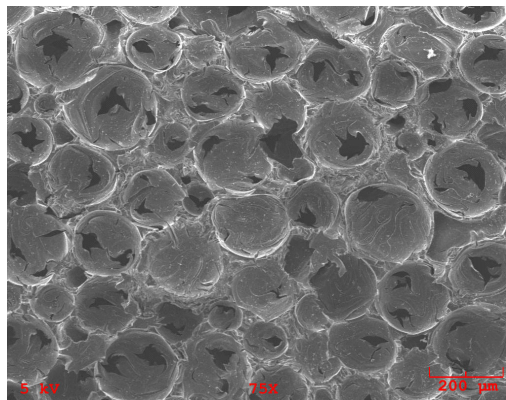


(b1) @310°C 75x

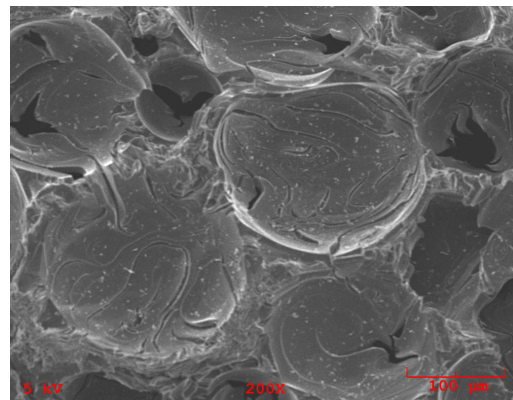


(b2) @310°C 200x

Figure 5.13: SEM Micrographs of Carbon Foam Produced at 310°C.



(c1) @320°C 75x



(c2) @320°C 200x

Figure 5.14: SEM Micrographs of Carbon Foam Produced at 320°C.

The last sample that is produced at 320°C can be seen in the Figure 5.14 above. It has a more uniform structure than the sample produced at 310°C, but the ligaments are not so clear comparing to the samples that were produced at 300°C.

5.4.2. Density Measurements Depending on the Mass / Volume Ratio

The change of density for the carbon foams produced at 300, 310, 320°C are shown in Figure 5.15. As seen from Figure 5.15 the densities increased to a maximum value at 310°C and dropped slightly for the case of the foam produced at 320°C. It is expected that the case of carbon foam produced by two stage process of stabilization and carbonization there would be a temperature ceiling after which foaming will start to deteriorate due to molten pitch loosing its strength to stretch and collapse. At 320°C it seems system is very close to this limit.

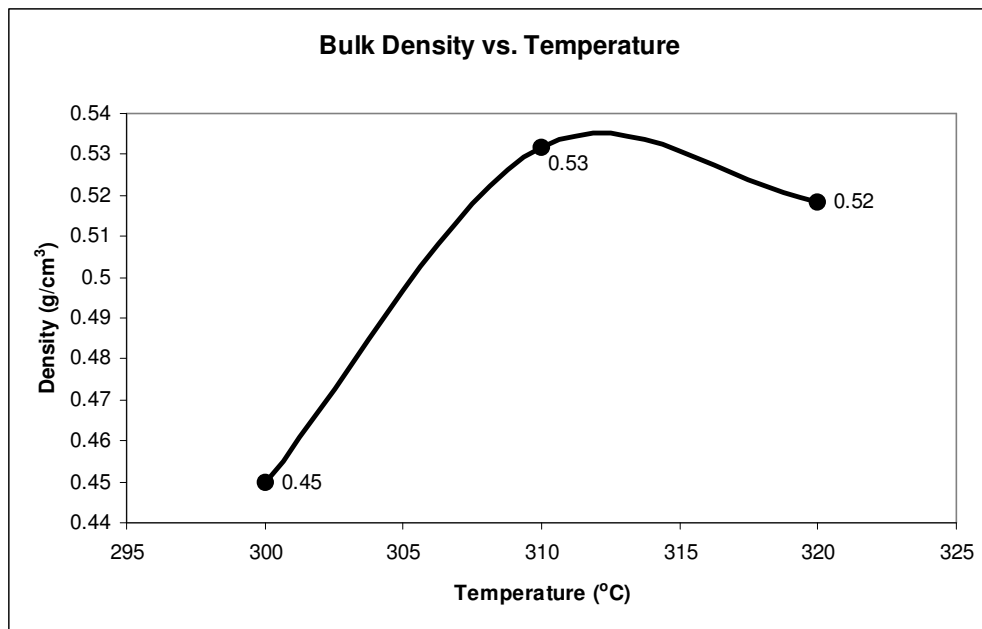


Figure 5.15: The graphic of the change in density of the carbon foam depending upon the production temperature.

5.4.3. Compressive Strength Analysis

Compressive strengths of the carbon foam samples obtained at 300, 310, 320°C are shown in Figure 5.16. From the figure it is observed that the strength of the foams increased with increasing processing temperature. At the highest temperature the density is not higher than the 310°C. Therefore, even though at the highest temperature the sample is not most compact but has the highest strength. This is at least in accordance with the electron micrographs which indicate a better foaming structure than the lower temperatures.

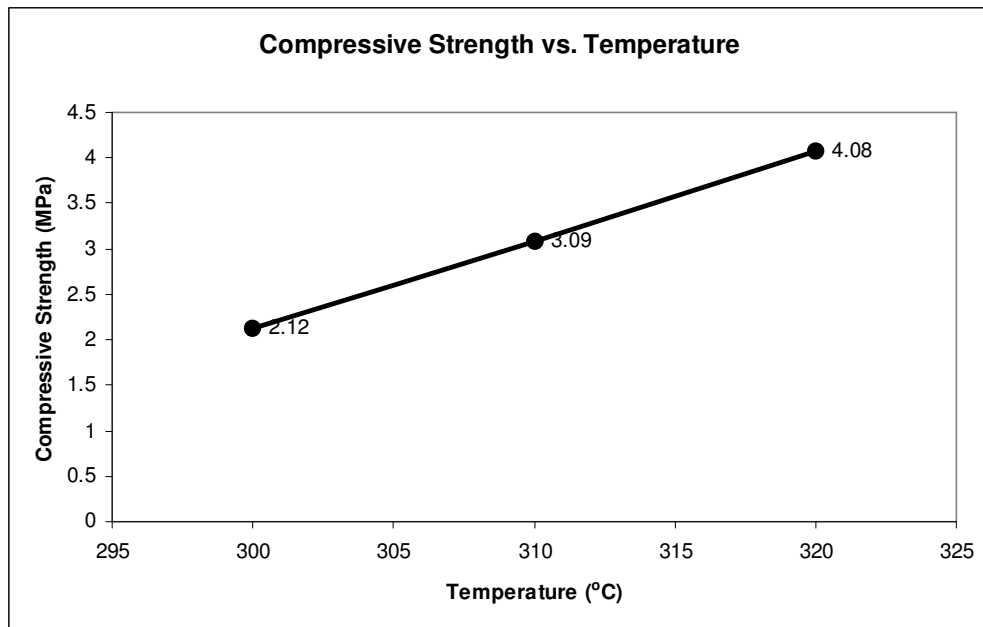


Figure 5.16: The graphic of the change in compressive strength of the carbon foam depending upon the production temperature.

5.5. The Effect of Softening Point of the Pitch in Carbon Foam Production

In this section the characterisation results of the carbon foam produced with three different precursors Ar251, EP050130 and 6T16 are examined. These precursors have different softening point values of 284°C, 251°C and 295°C, respectively. The carbon foams are produced at 300°C, 68 bar pressure and pressure released at a time of 5 seconds. The codes and the softening point values of the pitches can be seen in the Table 5.14.

Table 5.14 The codes and the softening point values of the pitches used in this study.

Code	Softening Point
EP050130	251°C
Ar251 (regular)	284°C
6T16	295°C

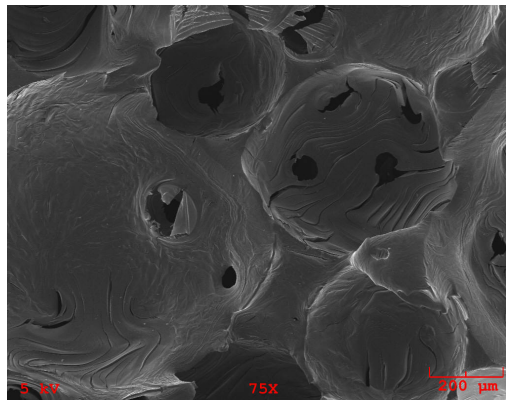
5.5.1. SEM Micrograph

The scanning electron microscopy micrographs of the carbon foams produced with three different precursors; Mitsubishi AR pitch regular (Ar251), EP050130 and 6T16 are given in the Figures 5.17, 5.18 and 5.19, respectively. In the Figures 5.17, 5.18 and 5.19; a1, b1 ,c1 are the SEM micrographs taken at 75 magnification for the samples produced with EP050130, Ar251 and 6T16 respectively and a2, b2, c2 are the SEM micrographs taken at 200 magnification for the samples produced with EP050130, Ar251 and 6T16 respectively.

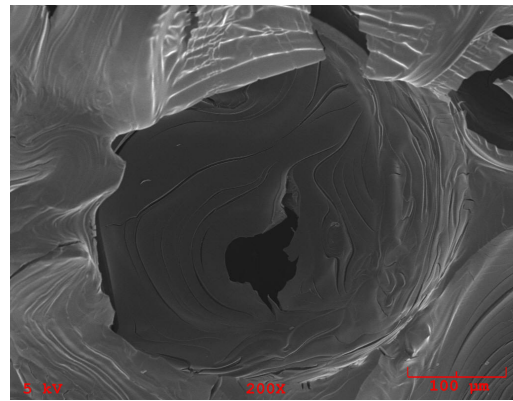
Carbon foam produced with EP050130, which has a softening point of 251°C, shown in Figure 5.17, indicate that the foaming characteristic of the sample is not uniform. This is indicated by the geometry of the cells which are non – uniform cells. The ligament boundaries are not well developed and a wavy structure is observed. This indicates the existence of non – uniform stacking of mesophase molecules.

The carbon foams obtained from EP050130 seems to have the graphene layers stacked and aligned but the cell and pore formation is not in place. The cells are not circular. There are some pores formed in some of the cells.

The standard foam is well described in the previous sections of the thesis. Comparing the foam produced using 6T16 mesophase with AR251 show that the foam obtained from 6T16 is developed more in terms of foaming. The cells are more uniform in sphericity. The pores are also more regular. The ligaments are formed in more distinct boundaries. However, there are also some pores which dominate the total domain of the cell indicating that there is an indication of easier pore formation.

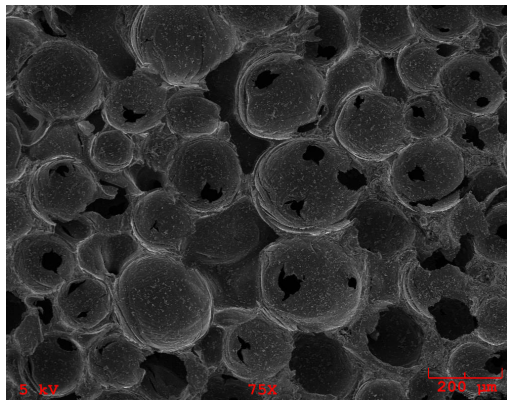


(a1) SP=251°C (EP050130) 75x

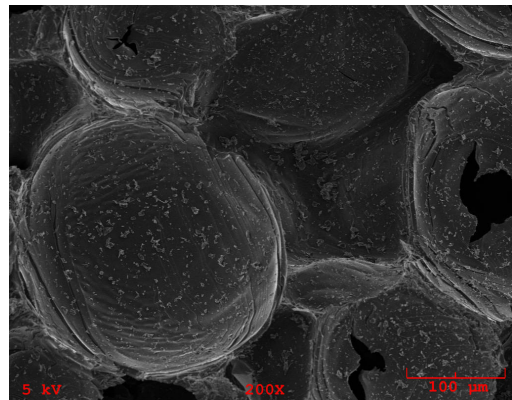


(a2) SP=251°C (EP050130) 200x

Figure 5.17: SEM Micrographs of Carbon Foam Produced with EP050130 mesophase pitch having softening point of 251°C.

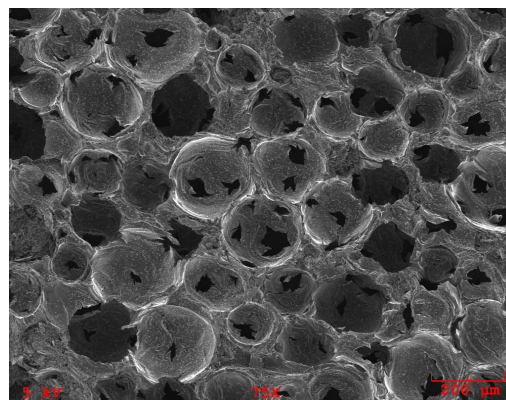


(b1) SP=284°C (Ar251-regular) 75x

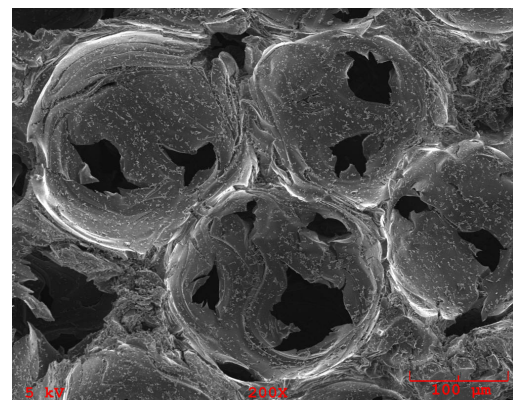


(b2) SP=284°C (Ar251-regular) 200x

Figure 5.18: SEM Micrographs of Carbon Foam Produced with Ar251-regular mesophase pitch having softening point of 284°C.



(c1) SP=295°C (6T16) 75x



(c2) SP=295°C (6T16) 200x

Figure 5.19: SEM Micrographs of Carbon Foam Produced with 6T16 Mesophase pitch having softening point of 295°C.

5.5.2. Density Measurements Depending on the Mass / Volume Ratio

The densities of foams produced from three different pitches having different softening points are given in Figure 5.20.

The density of EP050130 pitch is 1.27 g/cm^3 which is a reflection of the non porous structure of the foam which is mostly due to solid density. The density of the AR251 pitch is 0.45 g/cm^3 . The density decreases sharply to 0.13 g/cm^3 for the carbon foam produced with 6T16 mesophase pitch. This indicates the high porosity of the foam.

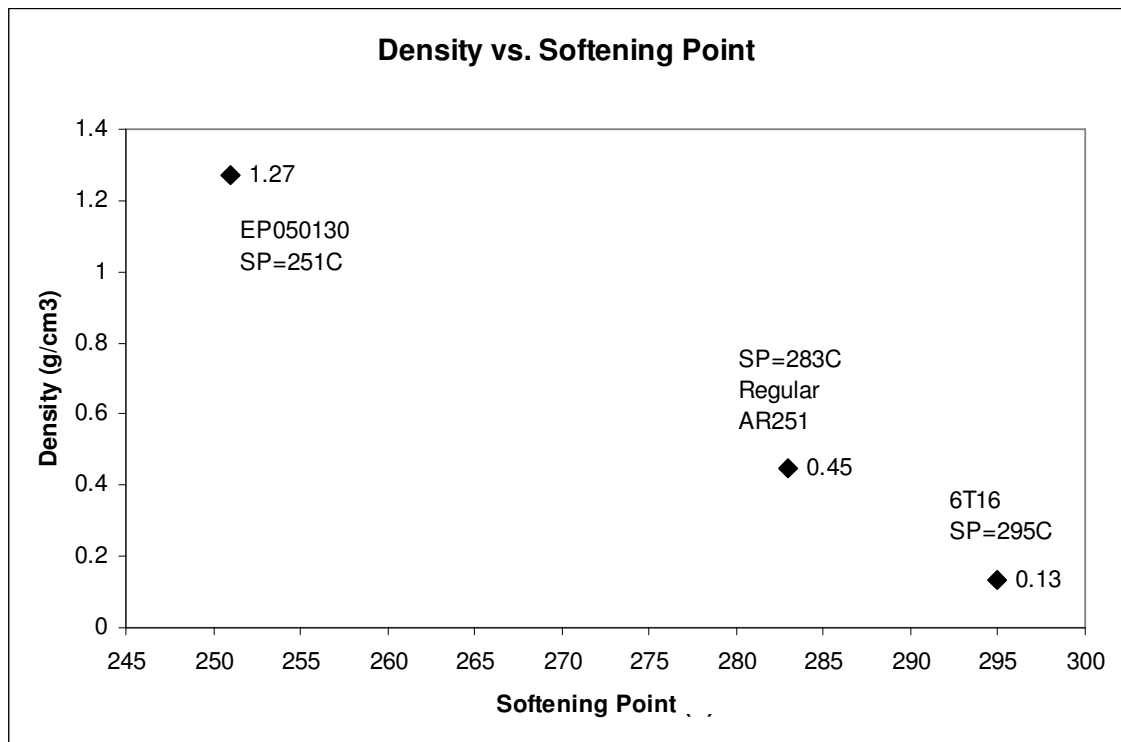


Figure 5.20: The graphic showing the densities of three different pitches having different softening temperature properties.

5.5.3. Compressive Strength Analysis

The comparison of compressive strengths between AR251 (SP=284°C) and 6T16 (SP=295°C) pitches are explained due to the improved foaming whereas the strength of EP050130 (SP=251°C) stems from the material difference. Therefore, the experimental condition for EP050130 should be optimized.

Investigation of the microstructure of three carbon foams produced from the three different precursors show that EP050130 has the lowest porosity. However,

comparing the compressive strength it is nearly as high as 6T16 pitch. The structural changes seem to add some mechanical capability to the foam produced from EP050130 pitch. Referring to the electro micrographs it is observed that the grapheme layers exhibit more transverse properties in the ligaments (5.17 a2) compared to 5.18 a2 and 5.19 a2.

In literature it is emphasized that foams gain strength from folding and zigzag structure since studies on carbon fibers showed that the zigzag morphology plays a key role in preventing glide of the 001 plane in graphitic material and enhances the tensile strength properties of carbons through an interlocking mechanism of grapheme layer [49]. If the carbonized foam were graphitized the interlocking mechanism will be enhanced.

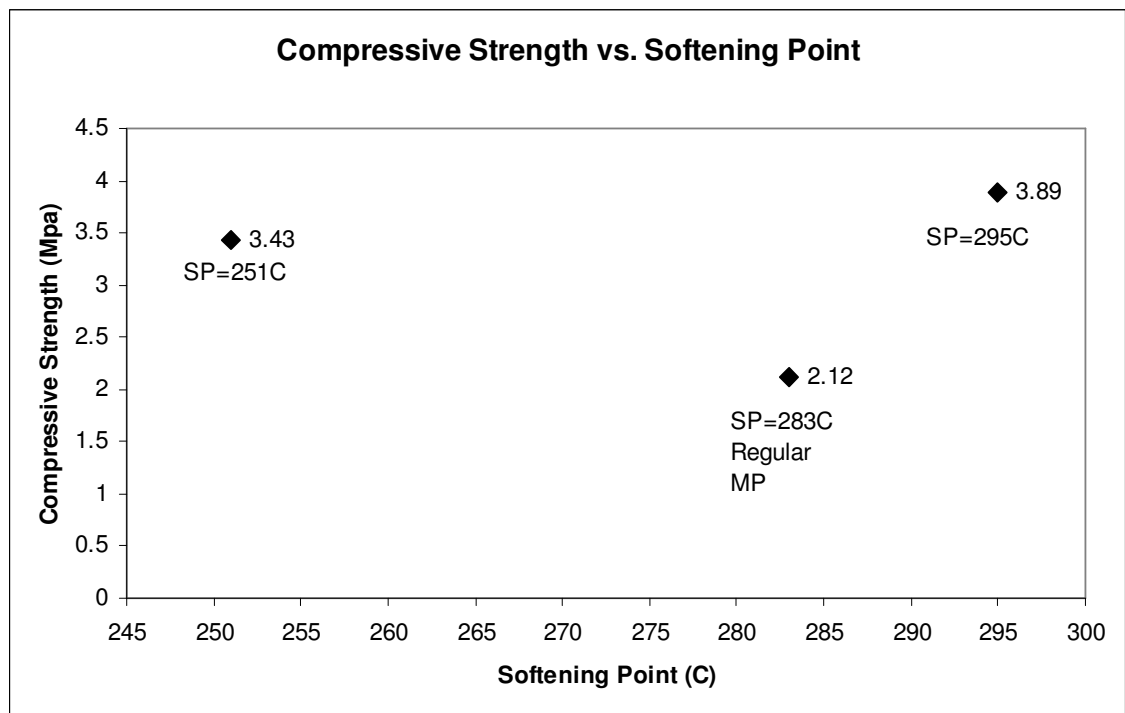


Figure 5.21: The graphic showing the compressive strength of three different pitches having different softening temperature properties.

5.6. Porous Structure by the Results of Mercury Porosimeter

Porosity of the samples is firstly calculated by the Equation 4.1. This equation uses the bulk density and solid density of the samples to reach a percent of porosity value.

Then, the mercury porosimetry is used. This instrument is used not only to get the percent of porosity values but also to have an idea of porous structure, pore diameter,

pore size distributions, total pore volume, total surface area, median pore and sample densities (bulk and skeletal)

5.6.1. The Effect of Boron Nitride on Porosity

In Figure 5.22 it is observed that the porosity of the carbon foams obtained with increased amounts of BN addition increased firstly, then decreased for the highest BN addition of 10 %. The increase in the porosity upto 1% BN is in agreement with the decrease in density measurements. Also the reduction in porosity at 10 % BN addition corresponds to a relative increase in density which indicates that the increase in the strength is not due to an improvement in the foaming mechanism.

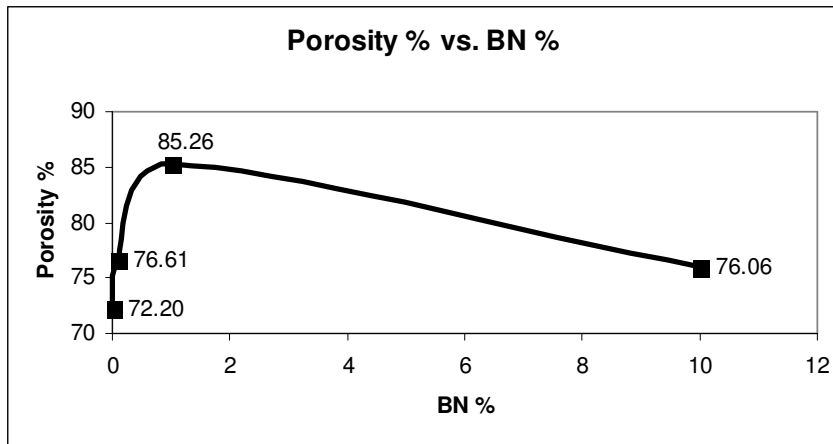


Figure 5.22: Porosity of the BN added carbon foam samples which are calculated by the Equation 4.1.

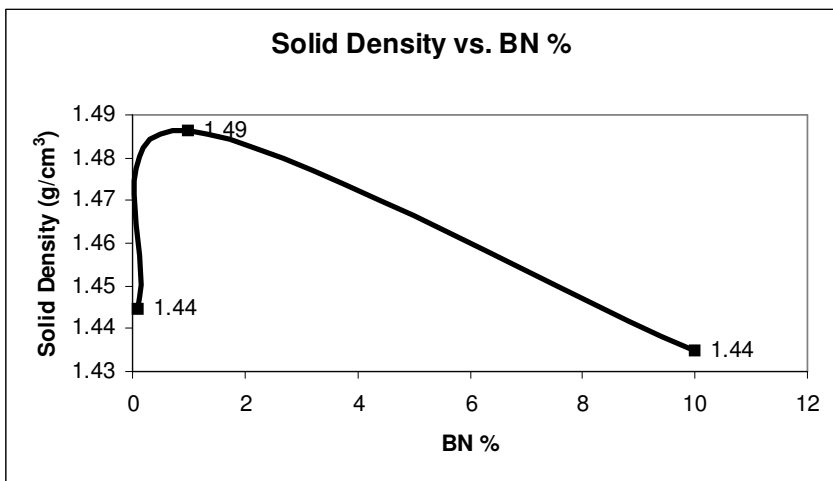


Figure 5.23: The graph of solid densities of BN added carbon foam samples

5.6.2. The Effect of Boron Carbide on Porosity

The effect of B_4C addition, resultant porosity and density of carbon foam are shown in Figures 5.24 and 5.25.

The behaviour of porosity and density of the carbon foam show similarity in which there are a sharp increase in 0.1 % and 1 % addition, followed by a drop at 10 % B_4C addition. This was also a similar behaviour to BN addition reported previously.

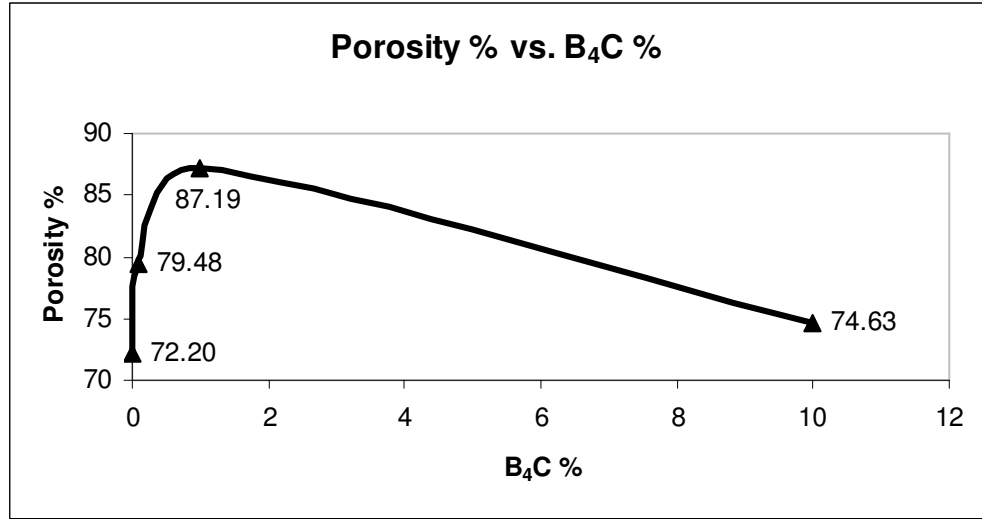


Figure 5.24: Porosity of the B_4C added carbon foam samples which are calculated by the Equation 4.1.

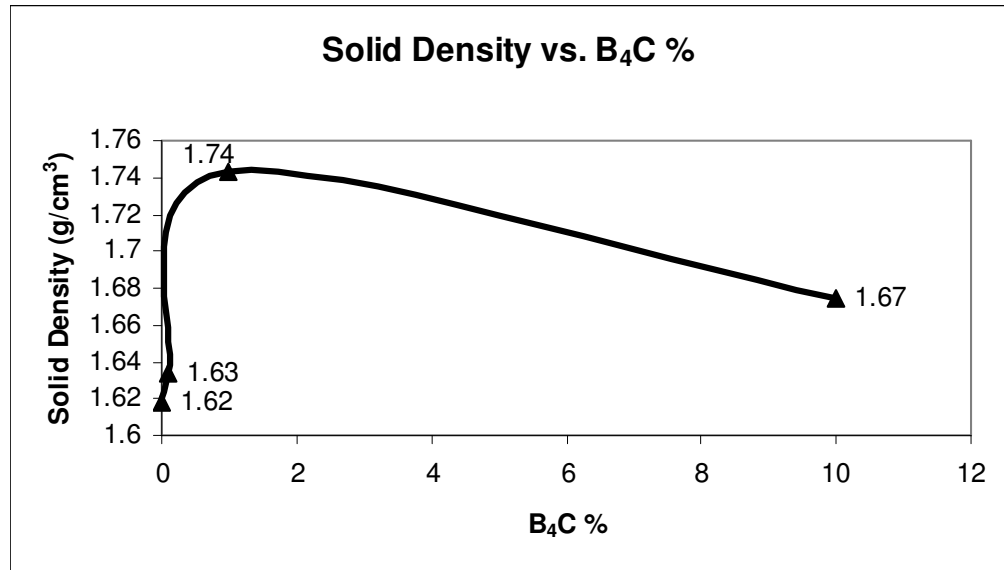


Figure 5.25: The graph of solid densities of B_4C added carbon foam samples.

5.6.3. The Effect of Temperature on Porosity

In Figures 5.26 and 5.27 the change in porosity and density of carbon foam produced at 300°C, 310°C and 320°C are shown.

Both porosity and solid density decreased when going from 300°C to 310°C and increased at 320°C.

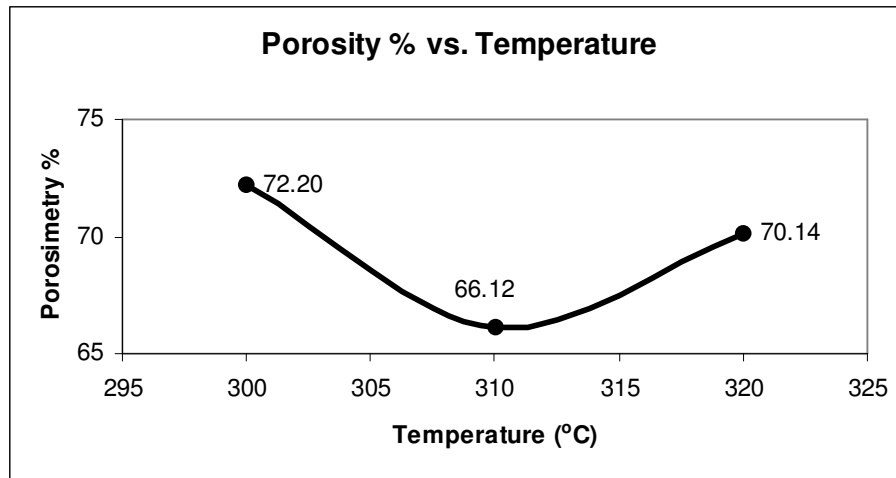


Figure 5.26: Porosity of the carbon foam samples produced at different temperatures which are calculated by the Equation 4.1.

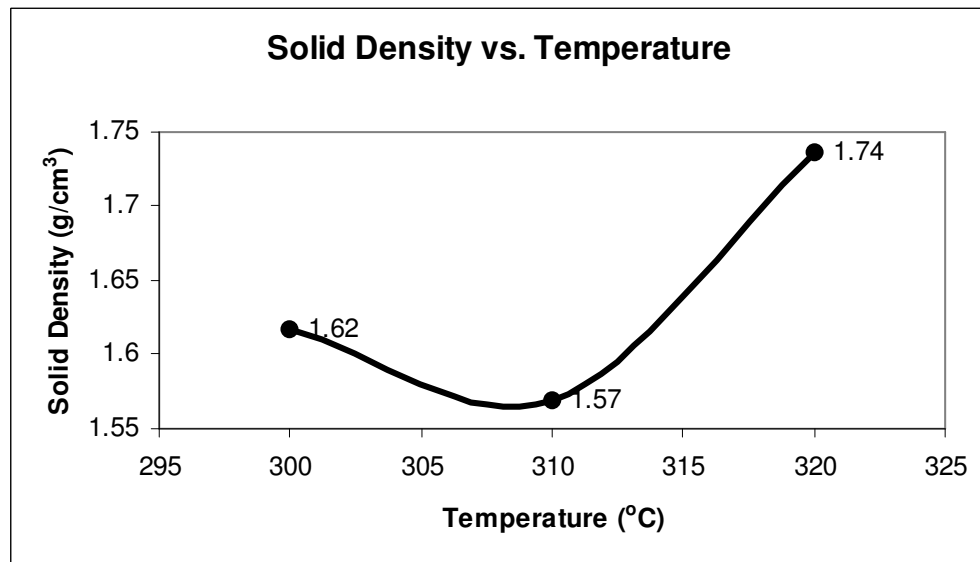


Figure 5.27: The graph of solid densities of carbon foam samples produced at different temperatures.

5.6.4. The Effect of Softening Point on Porosity

The relationship between the softening point of the foam precursor, porosity and density are shown in Figures 5.28 and 5.29. The porosity of carbon foam increased linearly with increasing softening point. Lower the density of the foam is increased from SP of 251°C to SP of 284°C and then decreased to a level of SP of 295°C pitch.

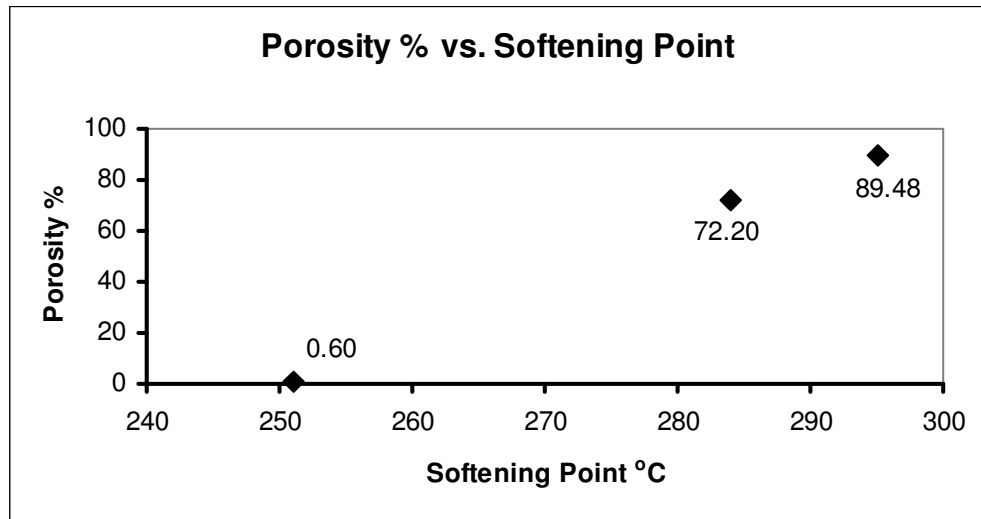


Figure 5.28: Porosity of the carbon foam samples produced with different pitches which are calculated by the Equation 4.1.

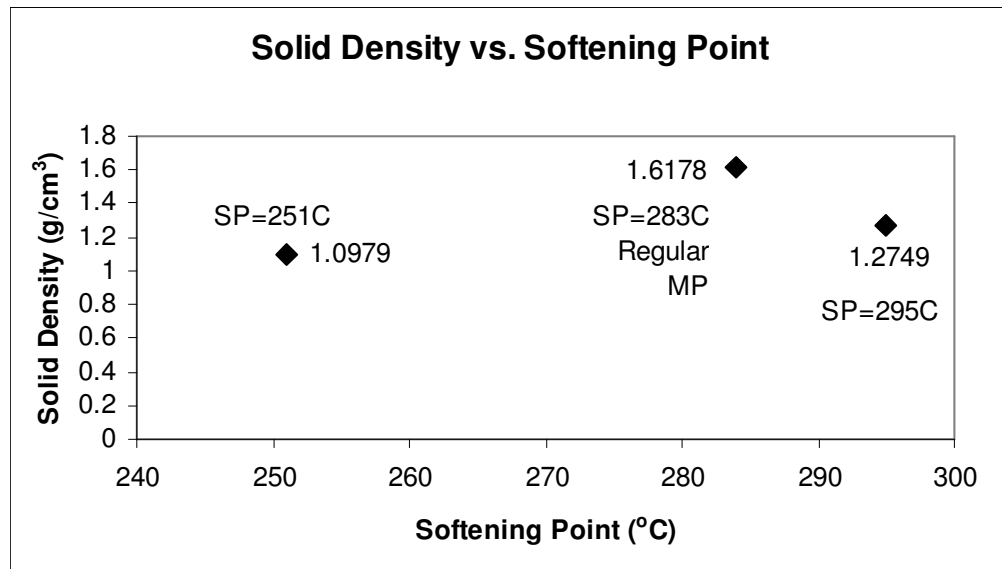


Figure 5.29: The graph of solid densities of carbon foam samples produced with different pitches.

5.7. Comparison of Effects of Boron Nitride and Boron Carbide Additives on Carbon Foam Production

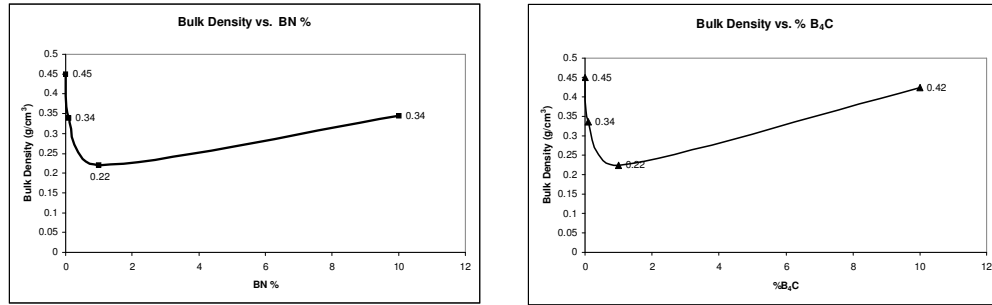


Figure 5.30: Graphs of the bulk densities of carbon foam with the ceramic additives (a) BN, (b) B₄C.

On the graphs above, in Figure 5.28, it is clearly seen that BN and B₄C has a similar effect on bulk densities of the foam produced. Bulk density is the density discussed in the previous sections which gives us the mass per unit volume for the whole part of the foam. In Figure 5.8 (a) we can see the change in bulk density of the foam depending on the addition of BN. In Figure 5.8 (b) we can see the effect of B₄C on bulk density of the foam.

Besides these, there is another point that should be discussed. That is the solid density which is determines the density of the solid part without the bubbles of the foam. We can reach the solid density values via helium pycnometry. The effect of BN and B₄C additives on the solid density of the foams produced are laid below in Figure 5.29.

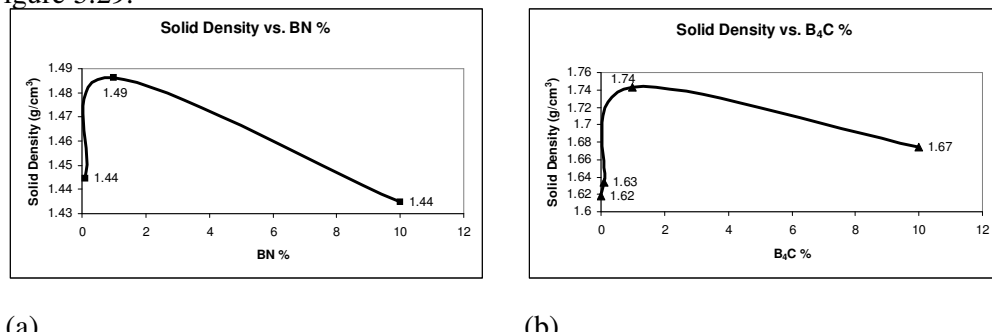


Figure 5.31: Graphs of the bulk densities of carbon foam with the ceramic additives (a) BN, (b) B₄C.

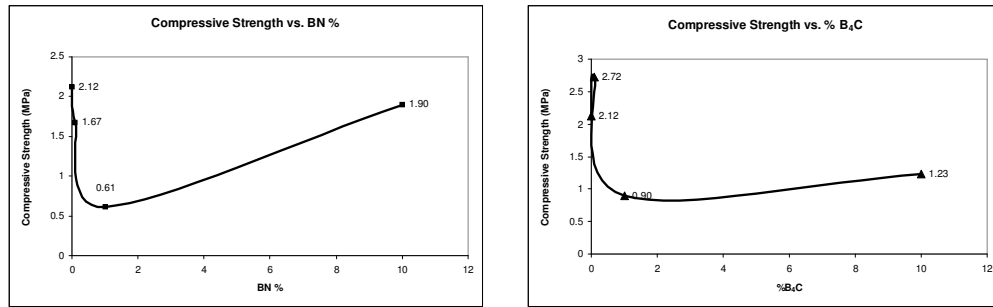


Figure 5.32: Graphs of compressive strength of carbon foam with ceramic additives (a) BN, (b) B₄C.

The compressive strength behaviours of carbon foams when BN and B₄C are added can be seen in the Figure 5.30 (a) and (b), respectively. Just like the bulk density behaviours of the same samples, the compressive strengths of the samples have an analogy between them. It is seen that not only the bulk density is directly affecting the samples, but also the addition of any ceramic materials containing boron might have the similar effect on the properties of carbon foam.

7. CONCLUSIONS

The addition of BN or B₄C to the pitch causes distinctive changes on the properties of the carbon foam produced. The changes of density and compressive strength have a similar trend both with the addition of BN and B₄C.

Addition of B₄C and BN resulted in an increase in porosity at lower levels and a decrease in the higher levels.

Minimum porosity and density values are obtained for 310°C carbon foam compared to 300°C and 320°C foam.

For the AR251 pitch increasing the processing temperature resulted in increased compaction (density) which leveled off at the highest temperature (320°C) indicating that the viscosity effect has reached to its maximum value.

Type of carbon foam precursor has a strong effect on the quality of foaming. The difference is attributed to the difference in the softening points.

The EP050130 pitch yielded carbon foam which possessed a different mechanism resulting in enhancement of material properties due to traverse structural formation. This results in an strengthened structure due to an interlocking mechanism.

REFERENCES

- [1] **Inagaki, M.**, 2000. Carbon Materials, *New Carbons: Control of Structure and Functions*, Elsevier, Tokyo, Japan
- [2] **Marsh, H.**, 1997. Carbon materials: an overview of carbon artifacts, *Introduction to Carbon Technologies*, pp.1-34, Eds. Marsh, H., Heintz, E.A., and Rodriguez-Reinoso, F., Universaded de Alicante, Secretariade de Publicaciones.
- [3] <http://pearl1.lanl.gov/periodic/elements/6.html>
- [4] **Edwards, I.A.S.**, 1989. Structure in carbons and carbon forms, *Introduction to Carbon Science*, pp.1-36, Ed. Marsh, H., Butterworths, London.
- [5] **Bourrat X.**, 2000. Structure in carbon and carbon artifacts, *Science of Carbon Materials*, pp.1-97, Eds. Marsh., Rodriguez-Reinoso, F., Universaded de Alicante, Secretariade de Publicaciones.
- [6] **Droege et. al.**, 1999. Low density open cell organic foams, low density open cell carbon foams, and methods for preparing same, *United States Patent*, No: 5945084 dated August 31, 1999.
- [7] **Edwards, I.A.S.**, 1989. Mechanism of formation of isotropic and anisotropic carbons, *Introduction to Carbon Science*, pp.1-36, Ed. Marsh, H., Butterworths, London.
- [8] **Klett, J.W., Gallego, N.C.**, 2003. Carbon foams for thermal management, *Carbon*, **41**, 1461-1466.
- [9] **Knippenberg, W.F., Lersmacher, B.**, 1976. Carbon Foam, *Philips Technical Review*, **36**(4), 93-103
- [10] **Arnold, J.R., Aubert, J.H., Clough, R.L., Rand, P.B. and Sylwester, A.P.**, 1989. Low-density microcellular carbon foams and method of preparation, *United States Patent*, No: 4832881 dated 23.05.1989.
- [11] **Vinton, C.S., Franklin, C.H.**, 1977. Method for the preparation of vitreous carbon foams, *United States Patent*, No: 4022875 dated 10.05.1977.
- [12] **ERG Materials and Aerospace Corporation** website, [http:// ergaerospace.com/rvc.htm](http://ergaerospace.com/rvc.htm)

- [13] http://www.industrialheating.com/CDA/ArticleInformation/features/BNP__Features__Item/0,2832,87444,00.html
- [14] **Bonzom et. al.**, 1981. Process for preparing pitch foams and products so produced, *United States Patent*, No: 4276246 dated June 30, 1981.
- [15] **Klett et. al.**, 2000. Method for extruding pitch based foam, *United States Patent*, No: 6344159 dated February 5, 2002.
- [16] **Klett et. al.**, 2000. Process for making carbon foam, *United States Patent*, No: 6033506 dated March 7, 2000.
- [17] **Sangwook, S., and Brian, P.R.**, 2003. Sandwich construction with carbon foam core materials, *Journal of Composite Materials*, **37**, 15, 1319-1335.
- [18] <http://www.ms.ornl.gov/ott/publications/sampe98.pdf>
- [19] <http://www.ms.ornl.gov/researchgroups/CMT/FOAM/foams.htm>
- [20] **Kearns, K.M.**, 1999. Process for preparing pitch foams, *United States Patent*, No: 5868974 dated 09.02.1999.
- [21] **Gencay, N.**, 2003. A mesophase pitch derived carbon foam: effect of pressure and release time, *Msc Thesis*, 22 – 27.
- [22] **Mochida et al.**, 1995. Carbon Fibers From Aromatic Hydrocarbons, *Chemtech*, p29 dated February 1995,
- [23] **Klett, J., Hardy, R., Romine E., Walls C., and Burchell T.**, 2000. High-Thermal-Conductivity, Mesophase-Pitch-Derived Carbon Foams: Effect of Precursor on Structure and Properties, *Carbon*, **38**, 7, 953-973.
- [24] **Brooks, J.D., and Taylor, G.H.**, 1965. The formation of graphitizing carbons from the liquid phase, *Carbon*, **3**, 185-193.
- [25] **Murdie et al.**, 1993. Carbon-Carbon Matrix Materials, *Carbon-Carbon Materials and Composites*, Noyes Publications, Park Ridge, N.J., 105-167
- [26] **Mochida, I., Korai, Y., Ku, C. H., Watanabe F., and Sakai Y.**, 2000. Chemistry of synthesis, structure, preparation and application of aromatic-derived mesophase pitch, *Carbon*, **38**, 2 , 305-328

- [27] **Mochida, I., Yoon, S.H., Korai, Y., Kanno, K., Sakai, Y., and Komatsu E.,** 2000. Mesophase pitch from aromatic hydrocarbons, *Science of Carbon Materials*, pp.1-97, Eds. Marsh., Rodriguez-Reinoso, F., Universaded de Alicante, Secretariade de Publicaciones.
- [28] **Murdie et. al.,** 2000. Process of making carbon-carbon composite material made from densified carbon foam, *United States Patent*, No: 6077464 dated June 20, 2000.
- [29] **Murdie et. al.,** 2001. Method of making pitch-based carbon foam. United States Patent, No: 6315974 dated November 13, 2001.
- [30] **Kearns et. al.,** 1999. Pitch foam products, *United States Patent*, No: 5961814 dated October 5, 1999.
- [31] **Klett, J.,** 2002. Pitch Based Carbon Foam and Composites, *United States Patent*, No: 6387343 dated May 14, 2002
- [32] **Klett, J.,** 2001. Pitch-Based Carbon Foam and Composites, *United States Patent*, No: 6261485 dated July 17, 2001
- [33] **Tan et. al.,** 2002. Microcellular carbon foams and microcellular C/C composites fabricated therefrom. United States Patent, No: 6339031 dated January 15, 2002.
- [34] **Hugh O.,** 1993, Handbook of carbon, graphite, diamond and fullerenes: properties, processing and applications. Noyes Publications, NJ, USA.
- [35] <http://periodic.lanl.gov/elements/5.html>
- [36] <http://www.feldcointernational.com/pagebrowse-58-103483.htm>
- [37] <http://www.pocothermales.com/faq.asp>
- [38] <http://www.historychannel.com/perl>
- [39] <http://encarta.msn.com>
- [40] http://www.china-superabrasives.com/images/CBN-series/CBN_borazon_A82_L.jpg
- [41] <http://hubacek.jp/bn/graphic/trBN.jpg>

- [42] <http://www.bornitrid.com/index.html?gclid=CLuJtsKJxYkCFQz-VgodW1nTOQ>
- [43] <http://131.104.156.23/Lectures/231/231%20pictures/boronnitride%20hexagonal.gif>
- [44] <http://131.104.156.23/Lectures/231/231%20pictures/boronnitride%20cubic.gif>
- [45] http://en.wikipedia.org/wiki/Boron_carbide
- [46] <http://www.feldcointernational.com/pagebrowse-58-103483.htm>
- [47] **Eksilioglu, A.**, 2004, Effect of temperature, solvent type and additives on the properties of mesophase pitch based carbon foam, *MSc. Thesis*, I.T.U., Institute of Science and Technology, Istanbul
- [48] **Gencay, N.**, 2003, Mesophase pitch derived carbon foam: Effect of pressure and release time, *MSc. Thesis*, I.T.U., Institute of Science and Technology, Istanbul
- [49] **Beechem, T., Lafdi, K.**, 2005. Novel high strength graphitic foams, *Carbon*, **44**, 8, 15548 – 1559
- [50] **Lo WL**, Deformations of foamed elastomers, *J. Cellular plast*, 1965, Jan, **45**, 59

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