THE EFFECT OF ADDITIVES AND PROCESSING CONDITIONS ON PROPERTIES
OF SINTERED MESOCARBON MICROBEADS

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Mesocarbon microbeads are an excellent precursor for high performance carbon materials because of their ability to self-sinter. The sintered product has many attractive properties such as high density, good thermal conductivity and high bending strength. However, the fracture properties need improvement for use in brake applications. To enhance the fracture properties, firstly, the carbonization behavior was systematically investigated and the processing conditions were optimized. Secondly, reinforcements, such as carbides and borides were introduced and the effect of heat treatment temperature on composite properties was studied.

Thermogravimetry-mass spectroscopy analysis proved that the chemical processes associated with hydrogen release are responsible for the major shrinkage event. Cracks formed during heat treatment when microbead pellets were compacted above 100Mpa. The oxidation pretreatment increased plasticity of the pellets and effectively eliminated crack formation. However, x-ray diffraction and microstructure analysis
indicated that the liquid phase sintering (<800K) that is critical to the development of “bridges” between microbeads, is prohibited, and the fracture properties decreased.

Eutectic liquid formed when a TiB₂/C composite was heat treated at 2800K or above, as evidenced by observation of a layered structure in the polished cross-section. At low TiB₂ loading, liquid phase sintering leads to a homogeneous distribution of TiB₂ particles in the carbon matrix of much smaller size and increased fracture properties. At higher loading, a complete transformation of mesophase carbon to graphite was observed and fracture toughness decreased. Diffusion of boron to the carbon matrix was proved by laser ablation ICP-MS. However, a control experiment indicates that it is not the main cause for the observed change in materials properties. Resistance to oxidation increased by more than two orders of magnitude due to TiB₂ additions. Fracture properties of the TiB₂/C composites increased further when finer TiB₂ powders were used, and eventually a composite with fracture toughness as high as 1.92MPa.m^{0.5} was obtained. Average pore size decreased by one order of magnitude for the best composite. Similar results were also obtained for TiC/C and ZrB₂/C composites but not for Ni/C composites, where the catalytic graphitization by nickel only leads to the formation of graphitic carbon. Further improvement maybe achieved by techniques such as hot-pressing to decrease the porosity level.
To my dear wife, Li Zeng
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CHAPTER 1:
CARBON/CARBON COMPOSITES AND THE OBJECTIVES OF THE PROJECT

Carbon is one of the most unique elements on earth. Carbon has the extraordinary ability to combine with itself and other elements, giving rise to a rich diversity of structural forms of solid carbon such as diamond, the materials with the highest hardness and thermal conductivity, and graphite, carbynes, fullerenes, etc.

Graphene-based carbon materials have found widespread applications in industry. They are produced in large-scale as electrodes for the steel and aluminum industry (million tons/year). Another important application is for C/C composites for the aerospace and aviation industry (1 billion dollars/year). Graphite is a highly anisotropic material. Within the graphene layers, the carbon atoms are linked by strong covalent bonds, resulting in an extremely high theoretical modulus of 1060 GPa, if loaded parallel to the graphene planes[1]. Carbon nanotubes, a graphene-based material, are the strongest material ever discovered. Recent measurement proves that their tensile strength can be as high as 63 GPa [2], very close to the theoretically predicted limit of 106 GPa. A carbon nanotube may be regarded as defect free, while large pores, on the scale of microns, are presented in traditional graphitic carbon material. The strength of porous graphitic carbon is very low, in most cases only of 10-30 MPa, and is controlled by internal defects following Griffith's theory. The mechanical properties of carbon fiber lie in between the
two extremes. During manufacturing, the graphene planes are aligned under tension (PAN fiber) and/or shear force (Pitch fiber).

Edison produced the first carbon fiber in the late 19th Century from regenerated cellulose (rayon) for use in incandescent lamps [1]. United Carbide produced the first commercial carbon fiber product from rayon in the early 1960s. The rayon carbon fiber was gradually replaced by the PAN fiber due to lower cost of the precursor fiber and better performance since its commercialization in 1969. Development of carbon fiber from pitch precursor took a much longer time. In the 1960s, it was found that carbon fibers manufactured from isotropic pitch have rather low strength and modulus. Production of high performance fiber was made possible due to the remarkable discovery of mesophase pitch by Brooks and Taylor in 1965 [3]. Graphitic pitch-based ultra high modulus carbon fiber became available in 1982. PAN fiber has better strength while pitch fiber has higher modulus.

The selection of carbon fiber and the fiber architecture play a dominant role in determining the characteristics of the C/C composite [1] [4]. Unidirectional composites have the highest efficiency of fiber packing and property translation, however, the out-of-plane properties are very poor and thus has no practical use. Laminar (2D) fiber architecture such as fiber felts and two-dimensional woven fabrics are easy to make, but the interlaminar strength is still governed by the matrix properties. The problem was solved by adding reinforcement in the third dimension and in the angular positions or along the diagonals in addition to the 3D orthogonal construction in the multi-directional (n-D, n>3) C/C composites. As the number of dimensions (n) increase, the fiber volume fraction in each in-plane direction decreases, resulting in decreased tensile and
compressive properties in those directions. However, off-axis properties, which are critical in applications under high thermomechanical loading such as being used as re-entry components, increase. Moreover, fiber volume fraction and the oxidation resistance increase. The disadvantages include the high cost of producing the fiber preform and increased difficulty of matrix impregnation. Chopped carbon fibers, generally 6-13mm in length, are the least expensive reinforcements and are widely used as reinforcements to molding compounds. They impart reduced shrinkage, greater stiffness, improved fatigue, etc. Chopped fibers are also used to produce fiber felts for brake manufacturing. As fiber length decreases, the load transfer becomes less efficient; however, traditional metallurgical methods may be used in the production.

The matrix materials bind the fibers together and act as load transfer medium as their moduli are much smaller. In addition, the matrix materials separate the fibers, prevent the catastrophic propagation of brittle cracks and protect the fibers from mechanical abrasion or chemical reaction with the environment. In C/C composites, the matrix materials are introduced by either chemical vapor deposition (CVD) of volatile hydrocarbon compounds such as methane, propane, or impregnation of liquid matrix precursor usually thermosetting resin or thermoplastic pitch. Theoretically, densification of the prepreg can be done in just a single step using the chemical vapor infiltration (CVI) process, while it usually takes 4-5 or more “impregnation-carbonization-graphitization” cycles to obtain fully densified product using the liquid impregnation approach. In general high carbon yield precursor materials (50-90%) are used in the impregnation. However, their densities are quite low, usually around 1g/cm$^3$, which are significantly less than the theoretical density of graphite, 2.26g/cm$^3$. In the isothermal CVD/CVI
process, it is desired that the deposition be reaction controlled rather than diffusion controlled, as the latter favors the formation of crusts on the outside surface that have to be removed by machining outside the reaction autoclave. Rapid surface reaction also leads to increased closed porosity, which serves to concentrate mechanical stress and thus is detrimental to the mechanical performance. The low reaction temperature (and deposition rate) results in an extremely long processing time. In most cases it takes more than one month and can be as long as 9 months for a single run. To decrease the processing time, a temperature gradient was introduced in the preform so that deposition only happens in a narrow zone and propagates steadily to the whole preform through temperature control. The thermal gradient method unfortunately is a single item processing technique and it is difficult to scale up. Various other techniques were also applied to increase the reaction rate, including the introduction of a pressure gradient, a pulse CVD method in which the autoclave was pumped to facilitate the release of the reaction product, a plasma enhanced CVD method in which the deposition happens at much lower temperature. However, only the isothermal and thermal gradient CVD methods were applied in commercial production. Although the cost of manufacturing is much higher for the CVD method, the mechanical performance is superior, especially the fracture properties, due to less stress accumulated along the fiber/matrix interface during manufacturing. In addition, in the CVD method, an oxidation resistant coating was created by conveniently adding precursor material to the gas stream while addition of the same materials to the carbonaceous liquid impregnant leads to severe fiber damage during heat treatment. The density attainable and thermal conductivity are much lower.
for products manufactured using the CVD/CVI process. In real production, the two methods are used together to make the process economically viable.

C/C materials have moderate mechanical properties, strength, modulus, etc, at room temperature. However, contrary to most engineering materials (super alloys, ceramics, etc), their mechanical properties increase a little with temperature, instead of suffering a dramatic decrease. This property combined with the extremely high melting point of graphitic carbon make C/C composites the materials of choice for application at temperatures higher than 2000ºC. Other attractive properties of C/C composites include low density, high thermal conductivity, low coefficient of thermal expansion, etc.

When C/C was first introduced to the Concorde supersonic passenger airliner as brake disks in 1973, the cost was around 550 pounds or 1000 dollars per kilogram. Due to the high manufacturing cost, its application was restricted to the military and aerospace field where the high cost is justified by the improved performance. The other factor that is responsible for the limited application of C/C composites is the susceptibility to oxidation, which starts below 500ºC in air and is limited only by the diffusion rate of oxygen at 800ºC. The fiber/matrix interface is attacked first and fiber bundles are weakened. Two approaches have been used to solve the problem. One is to use inhibitors such as boron, phosphorous and silicon. The other is to use a diffusion barrier to prevent the composite from reaction with oxygen. Borates are the most effective inhibitor as they form a glass layer that has the appropriate viscosity to seal the matrix inner and surface cracks. Unfortunately, boron oxide has relatively high vapor pressure and is lost at temperatures higher than 1000ºC. Silicon-based ceramic coatings provide protection up to temperatures of 1700-1800ºC. However, they have significantly higher coefficient of
thermal expansion than C/C and result in crack formation during thermal cycling. Multilayered and gradient coating systems were developed to alleviate the thermal stress.

According to G. Savage, some 63% by volume of C/C composites manufactured were used in aircraft brake system [4]. Carbon materials are well suited for friction applications. Besides good wear properties, for aircraft brake applications it is essential to have reasonable heat capacity and very good thermal conductivity. A Boeing 767 at a take-off speed of 320km/h has a kinetic energy of 670MJ[5]. During aborted take-offs this energy must be dissipated in 30s by the eight brakes of the aircraft. As a result, temperature of the frictional surface may rise to more than 2000ºC in a very short time, which is enough to melt metal components. As a structural component, the aircraft brakes must have sufficient mechanical properties, especially fracture property, to generate the required torque. The C/C composites have a heat capacity that is 2.5 times that of steel. The thermal conductivity is comparable or better than steel depending on the manufacturing method. They have very good fracture properties and the superior mechanical property is maintained at such extreme temperatures. In addition, the density of a C/C composite is around 1.9g/cm³, compared to 7.8g/cm³ for steel. The introduction of C/C composite brake disks leads to up to 60% weight savings [6] and doubled service time compared with metal brakes. A detailed review on the wear behavior are presented by Blanco et al. [7].

Honeywell is one of the leading manufacturers of aircraft brakes. In an effort to decrease the manufacturing cost, high-density carbon pellets made from mesocarbon microbeads were investigated as an alternative. Mesocarbon microbeads are carbonaceous fine powder produced from pitch precursors. During heat treatment, the
pellets made from mesocarbon microbeads shrink isotropically so that carbon product with porosity as low as 5% can be produced in a single step [8]. Honeywell engineers found that the friction and thermal properties of the pellets were good; however, fracture toughness of the materials was unacceptably low as the pellets fractured into pieces during testing. As the raw material is in the powder form, the method of sample preparation and processing is essentially the same as traditional powder metallurgical methods. In the field of ceramics, it is a common practice to improve the mechanical properties by addition of reinforcements in the form of powder, fiber or whiskers, to provide “crack tip shielding” so that the effective stress intensity factor experienced in the near-tip region is reduced from the far-field value [9]. In this project, we attempted to improve the fracture properties of the pellets made from mesocarbon microbeads by the addition of appropriate reinforcements and optimization of the processing conditions.

The thesis is divided into several parts. In Chapter 2, a review of the literature study relevant to our objective is presented, with the focus on production and sintering behavior of mesocarbon microbeads as well as the effect of additives. Experimental procedures are summarized in Chapter 3. In Chapter 4, the carbonization and graphitization behavior, i.e., weight loss, off-gas composition, shrinkage behavior, evolution of crystal structure and microstructure, fracture property, etc, was studied systematically. In Chapter 5, TiB$_2$ was introduced as a particulate reinforcement. The evolution of materials properties as a function of heat treatment temperature was thoroughly investigated with a focus on the property change around the eutectic liquid formation temperature. In Chapter 6, several other carbon composites which are capable
of forming eutectic liquid were studied in a similar procedure. The experimental results are summarized in Chapter 7 together with recommendations for future research.
2.1. Mesophase Carbon

2.1.1. Mesophase Formation

Heat treatment of highly aromatic feed stocks (i.e. several condensed rings per cluster), such as petroleum pitch, coal-tar pitch, etc, at temperatures between 350-500ºC leads to the formation of an optically anisotropic liquid crystalline phase, *mesophase carbon*, from the isotropic parent pitch. The formation of mesophase can be divided into several steps. First of all, polycondensed aromatic molecules form due to thermal decomposition and thermal polymerization reactions. As the molecules grow larger, the cohesive force exceeds the translational energy, the alignment of lamellar molecules results in the formation of nematic discotic liquid crystals[10]. The mesophase adopts spherical shape to minimize surface energy. With an increase in retention time or reaction temperature, the spherules coalesce to form larger spheres, and eventually, phase inversion occurs as the mesophase becomes the continuous phase, i.e., bulk mesophase. Heat-treated pitches containing mesophase spherules or bulk mesophase are named mesophase pitch[11]. The mesophase spherules can be separated from the isotropic pitch matrix by solvent extraction. The mesophase spherules separated as quinoline insoluble (QI) from the mesophase pitches are named mesocarbon microbeads (MCMBs) [11].
High temperature centrifugation was also applied to separate mesophase spherules as mesophase is denser than the isotropic phase[12].

The formation of mesophase can be thermally activated or with the help of a catalyst such as ferrocene[13] [14]. The growth of liquid crystals is similar to crystallization, beginning with nucleation and continuing through the complete conversion to mesophase[1]. Addition of carbon black particles was found to effectively inhibit coalescence of the mesophase spheres and give the MCMB uniform morphology[15].

Mesophase carbon is generally produced from pitch precursor materials such as petroleum pitch or coal-tar pitch. The only synthetic mesophase pitch was produced by Mitsubishi Gas Chemical Company from naphthalene/alkyl-naphthalene[16]. The synthetic AR pitch has a very low softening point and viscosity at its molten stage, and thus can be used to impregnate carbon fiber performs [17] [18] [19]. It is 100% mesophase and has a very high coking value: 80-85% at ambient pressure.

The mesophase transformation in the liquid phase carbonization was first recognized by Brooks and Taylor in 1965[3]. Several models have been proposed to describe the structure of the mesophase spherules, with schematic representations of the models available in the review written by Mochida et al.[12].

2.2. Sintering Behavior

Traditionally, synthetic graphitic materials were produced by using pulverized coke as a filler and pitch as a binder [20]. The baking and impregnation procedures have to be repeated several times to achieve sufficient strength. They are expensive and very time consuming. The sintering of mesocarbon microbeads, however, requires no external
binder phase as the beta resin, or the toluene insoluble (TI) and quinoline soluble fraction, acts as an *in situ* binder. High performance carbon artifacts can be produced in a single, fast sintering operation.

2.2.1. *Mesocarbon Microbeads*

The fact that powdered polyaromatic mesophase can be used to produce fine grained isotropic carbon was known to the scientific community as early as the mid-1980s. Dr. Huttinger’s group made major contributions to our understanding in the synthesis and sintering behavior of mesophase carbon in the 1990s. In 1993, Hoffmann and Huttinger demonstrated the spontaneous liquid-phase sintering of mesophase powders using the *Curie* point technique, in which the samples were shock-heated to the *Curie* temperature of the induction coil [21]. The viscosity of the sinterable mesophase was found to firstly decrease with the increase in temperature and then increase. The decrease is a net physical effect and is reversible while the increase is caused by chemical reactions and is irreversible [22]. Since viscous flow is the main driving force, the *Curie* point technique is adopted to minimize the impact of chemical changes and maximize the liquid phase sintering. Later the sintering behavior of two mesophase powders, with one of them being sifted into three different sizes, was subjected to systematic investigation [23]. It was found that volume shrinkage of the initial liquid phase sintering is much smaller compared with solid phase sintering. An appropriate pre-sintering step was found critical to the development of mechanical properties during which pyrolysis reactions gradually opened the pores closed by the liquid phase sintering. The authors suggest that better materials properties can be obtained using finer mesophase powders. The authors
also gave a schematic description on the evolution of volatile matter and made connection among hydrogen elimination, shrinkage and development of crystal structure. Pore volume was found to maximize at around 800°C and 1600°C as shown in Fig. 2.2. Graphite materials with flexural strength as high as 160MPa were obtained after graphitization heat treatment at 2400°C. Maximum flexural strength was achieved at a heat treatment temperature of around 1200°C for all microbeads.

The importance of liquid phase sintering was also recognized by Nagayama et al. [24]. It was concluded that sintering in the liquid phase proceeds through fusion by the beta resins between 400°C and 600°C. The self-sintering behavior of mesocarbon microbeads was further confirmed by Gao et al. [25] and Bhatia et al. [26]. The authors observed large variation in weight, volume, conductivity and C/H ratio during the early stages of solid phase sintering at temperatures between 600°C and 1000°C. Bhatia et al.,
indicate that open porosity of the pellet has a minimum and mechanical properties (bending strength, hardness) peak at temperatures around 1000°C. The development of crystal structure of Osaka Gas microbeads, as indicated by the variation in \(d_{002}\) spacing of graphite phase and \(L_c\), was studied by Haridoss et al.[27] in the temperature range 400-1100°C. The solid phase sintering was characterized by an initial increase in turbostratic disorder and the order was regained at heat treatment temperatures higher than 800°C. Interestingly, an increase in crystallite size was observed when the microbeads were heat treated around 400°C. The authors attribute the change to the release of impurities originally presented as layers between the graphitic layers. The mesophase composition (TI, beta resin, etc) was adjusted by extraction/washing using toluene by Martinez-Escandell et al.[28]. It was found that while appropriate washing/extraction reduces the chance of swelling due to excessive fusibility, excessive washing/extraction decreased the beta resin content and the ability of the mesophase powders to self-sinter. A similar result was obtained by changing the mesophase composition through low temperature calcinations[29]. The shrinkage behavior of Osaka Gas microbeads was characterized using dilatometer by Norfolk et al. [8]. The sintering process was described as consisting of two separate processes: neck formation as a result of non-densifying liquid phase sintering at temperature < 800K and rapid sample shrinkage due to changes of theoretical density in the temperature region 800-1200K resulting from crystallographic rearrangement. The rapid sintering stage was thought different from the conventional solid state sintering as the activation energy approaches zero. In high temperature graphitization study they measured an activation energy of merely \(~100\text{kcal/mol}\), compared with \(~240\text{kcal/mol}\) for thermally activated graphitization
of typical carbon systems[8]. The authors attribute this to the preferred orientation of graphene planes within the microbeads.

2.2.2. Mesophase Pitch

Milled mesophase pitch is also a good precursor material for high performance carbon artifacts. The sintering behavior is similar to that of mesocarbon microbeads, but mesophase pitch in general has excessive fusibility and because of this, mild oxidation pretreatment is required to prevent “bloating” during early stage of sintering. Drbohlav and Stevenson studied the oxidation and sintering behavior Mitsubishi mesophase pitch. FTIR was used to characterize and quantify oxygen functionality present in the oxidized pitch. It was concluded that the initial weight gain involves the loss of aliphatic content and a concurrent formation of predominately ester and anhydride functionality, while the weight loss at higher temperature involves the loss of aromatic carbon[30]. The carbonization behavior of the original and oxidized pitch was studied using thermal volatilization analysis/sub-ambient thermal volatilization analysis (TVA/SATVA), in which volatiles emitted from thermal analysis passed through an acetone/dry ice slurry (-75°C), liquid nitrogen (-196°C) and 5 angstrom molecular sieve[31]. The volatile materials trapped were distilled and characterized by FTIR. It was concluded that carbonization of unoxidized pitch is accompanied by the production and subsequent rearrangement, migration and recombination of large quantities of oxygen free aromatic radicals and the dimensional stability of the oxidized pitch is attributed to the concerted decarboxylation reactions which result in “caged” aromatic radicals that are advantageously positioned for recombination without migration or rearrangement. Fanjul
et al. studied the oxidation and carbonization of both coal-tar and naphthalene based mesophase pitch. Similarly, the oxidation stabilization was found to be a dehydrogenative process where the hydrogen removed is predominantly aliphatic and the oxygen uptake is mainly in the form of ester and anhydride functionality[32, 33]. Oxidation stabilization in air at temperatures of 225 and 250ºC was found to be most appropriate. Naphthalene based mesophase stabilized more easily but the stabilization process was more difficult to control. Excessive oxidation of coal-tar pitch based mesophase leads to an increase in weight loss, temperature of the weight loss, porosity and a decrease in contraction [34] [35] while the trend is not obvious in the naphthalene based mesophase pitch. The mechanical and electrical properties increase with the increase in molding pressure[34]. The authors concluded that sinterability of the stabilized sample was mainly governed by the plasticity, which can be characterized by the “pushing-rod” experiment. The oxidized pitch samples were compacted uniaxially and heat treated at 9 different temperatures between 400-2600ºC[36]. The authors found porosity mainly appears below 800ºC, during the low sintering phase and at the initial stage of solid phase sintering and it decreases with further densification. Flexural strength peaked at a heat treatment temperature of around 1000ºC while electric conductivity increased further at higher heat treatment temperatures. Fujiura et al. prepared some extremely fine naphthalene based mesophase pitch powders (average size 2.4 µm) by jet milling. They used low temperature heat treatment to adjust volatile matter and remove the excess fusibility[37, 38]. Mechanical properties increased significantly with a decrease in particle size. The average pore radius of pellets heat treated at 2400ºC was found to be only 0.03µm.
Many authors mentioned the importance of slow heating rate in low temperature heat treatment as a lot of volatile matter evolved in this stage. For mesophase carbon synthesized from high sulfur containing precursors such as petroleum pitch, a slow heating rate is also required in the temperature range from 1300-1800ºC to abate the damage caused by sulfur puffing[13]. The graphitic materials originating from petroleum become more and more important, particularly in the US because of stringent environmental restrictions. The extent of puffing was suppressed with the impregnation of inhibitors[39].

2.3. Effects of Additives

2.3.1. Carbon Fiber/Graphite Flakes

The self-sintering ability of mesophase carbon is so attractive that, not surprisingly, investigations were carried out to make C/C composite from mesophase carbon. However, the large shrinkage of mesophase carbon materials means the easy approach, relatively low temperature hot-pressing followed by pressureless sintering, is impossible for making long fiber reinforced carbon composites. On the other hand, mesophase pitch has appropriate flow properties at temperatures above 200ºC[40] and thus is suitable for use as impregnation material[41] [19]. Oxidation stabilization is required to retain the mesophase pitch within the fiber preform.

Gao et al. prepared C/C composite using mesocarbon microbeads as the matrix[42]. The microbeads were mixed with ground pitch fiber (400 µm in length), hot-pressed at 250MPa at 150ºC, and then heat treated to 1000ºC. The authors found
density and bending strength of the composite decrease notably with the increase in carbon fiber content. However, composites made from preoxidized fiber (by nitric acid) and microbeads (250°C in air) have better properties than pellets made from microbeads alone. The carbon fiber used in the study has a tensile strength of only 241MPa. Hu et al. used aqueous tape casting to make C/C from PAN-based short carbon fiber (100, 200, 400 µm) and MCMBs made from coal-tar pitch[43]. In all cases, the authors saw significant decreases in shrinkage, density, bending strength and electric conductivity.

Graphite flakes were used by Mirhabibi et al. as reinforcement of pellets made from MCMBs. The raw materials were mixed homogeneously, cold pressed and then heat treated to 1500°C. They found that porosity increased, strength and modulus decreased with the increase in graphite flake content. However, the work of fracture, determined as the area under the load-displacement curve, increased significantly[44]. Graphite flakes were found to be aligned perpendicularly to the surface. In a later publication, the authors claim that for the same materials, both fracture toughness and Weibull modulus increases by a factor of 2-3 with around 10 vol.% graphite flake addition. It is worth noting that, as the authors described in the experimental section, the initial notch was perpendicular to the general plane of the orientation of the graphite flakes[44].

2.3.2. Carbides

Garcia-Rosales et al. studied the doping of B₄C, TiC, VC, ZrC and WC on the thermo-mechanical properties of pellets made from petroleum residue based MCMBs [45]. The MCMBs were jet-milled to 2.6 µm and very fine carbide powders, 1 µm or smaller were used in the experiment. The raw mixture was cold pressed and then sintered
up to 2900ºC. The authors found all carbides act as catalysts for the graphitization of microbeads and the catalytic ability as measured by the lowest graphitization temperature (initiation temperature of Lc growth) follows the same trend as the corresponding eutectic liquid formation temperature. Thermal conductivity increases proportionally with the increase in Lc. However, the thermal conductivity of B4C doped pellets decreased, possibly due to phonon scattering. Flexural strength, Young’s modulus and fracture toughness (Kic) as determined by a Vickers indentation test follow a similar trend. WC and ZrC were found to increase the mechanical properties at temperatures higher than 1500ºC, while for pellets with TiC and VC additions, the mechanical properties decrease. Liu et al. investigated the effect of Ti additions on shrinkage and performance of pellets made from petroleum residue based MCMBs[46]. The raw mixture was cold pressed and sintered to 1300ºC. Shrinkage decreased continuously with Ti additions while flexural strength, electric conductivity and the extent of graphitization peaked at 7.5wt% Ti addition. Total porosity increased while open porosity decreased with Ti additions. Hu et al. prepared Ti, ZrO2 and B4C doped MCMBs (coal-tar pitch based) using aqueous tape casting[47]. The green tape was hot-pressed at 85ºC, 100MPa and then vacuum sintered to 1400ºC. All three additives act as catalysts for the graphitization process with Ti as the most effective one. Bending strength and electric conductivity increased continuously with the increase in Ti content up to the tested maximum. For pellets with B4C and ZrO2 additions, the best properties were obtained at 5 wt.% addition. Norfolk et al. studied the shrinkage behavior of Si doped Osaka Gas microbeads[8]. The green pellets were cold pressed and sintered to 1500ºC. The authors found the exothermic reactions (Si+C or Si+N2) lead to sample swelling. Silicon-containing polymer was also investigated as a
SiC precursor and it was found to increase the linear shrinkage. The silicon containing polymers were known to decompose to give nanosized SiC particles when heat treated above 1650°C[48]. No results on mechanical properties was reported though.

In some research MCMBs weren’t used as a matrix material but still they are relevant to this topic. Zhang et al. prepared Ti, Ti-Si and B₄C-Ti-Si doped graphite from a petroleum coke[49]. The powders were bound with coal tar pitch and hot pressed to 2200°C and 2600°C under 30MPa. The best materials properties were obtained with 7-11wt. % Ti additions. The extent of graphitization was greatly enhanced with the addition of Ti and/or Si. A very high thermal conductivity, 350W/m K, was observed for Si-Ti doped graphite, while for pellets with B₄C additions thermal conductivity decreases. The bending strength increased significantly with B₄C additions. Si was found to be depleted upon heat treatment at 2200°C, resulting in the formation of cavities and a decrease in mechanical properties. Raman et al. prepared carbon-ceramic composites (C-SiC-B₄C) using a coal-tar based green coke as the matrix material[50]. The mixture was cold pressed and sintered to 2200°C. The composite showed improved oxidation resistance at 800-1200°C due to the formation of a glassy protective coating. A similar result was reported by Ogawa et al.[51]. The authors believe the formation of SiO₂-B₂O₃ eutectic solution is critical to the high temperature oxidation resistance. Boron oxide melts around 450°C. Its formation is responsible for the low temperature oxidation resistance, but its vapor pressure is too high at temperatures greater than 1000°C.

Many carbides, such as Fe₃C, Cr₃C₂, Mo₂C and VC act as catalysts for graphite oxidation[52]. ZrC and TaC form stable nonreducible oxides that are not catalytically
active. The carbide-catalyzed graphitization was believed to proceed via a solution-precipitation mechanism[53].

2.3.3. Boron and Boron Containing Compounds

Boron has a fairly large solubility in graphite, 2.35 at.% at 2350°C forming a substitutional solid solution [54]. $^{11}$B-NMR experiments proved that isolated boron atoms are dominant at low boron concentrations[55]. Eutectic liquid forms at 2245°C [56]/2375°C [54] in B$_4$C/Graphite mixtures with ~30 at.% total C content.

Boron is a good graphitization catalyst. At low concentration (1wt. %), boron only accelerates the homogeneous continuous graphitization. At higher concentration, (≥ 5 wt.%), a turbostratic component appears in non-graphitizable carbon precursors at 2200°C and a graphitic component appears in both graphitizable and non-graphitizable precursors at 2400°C[10]. Note that the temperatures are in fairly good correlation with the eutectic liquid formation temperature.

As mentioned in the previous section, for hot-pressed carbon pellets, B$_4$C addition leads to increased bending strength and lowered thermal conductivity [49]. Similar results were also observed by Guo et al.[57]. The composite was prepared using the same procedure except that boron substituted mesophase pitch was used as a binder and coke powders as filler. Wolf used NaBO$_2$ as the boron source to impregnate pellets sintered from mesocarbon microbeads [59]. The author observed significant increase in bending strength, ~120MPa at 10wt% boron loading compared with ~90MPa of the original sample [58]. Becker et al. synthesized boron-substituted mesophase pitch powder by co-pyrolysis of a coal tar pitch with pyridine-borane [59]. The milled mesophase powder
was cold pressed and pressureless sintered up to 2000°C. The authors observed an increase in the extent of graphitization at temperatures higher than 1800°C. However, mechanical properties decreased by increasing the boron content from 0.5% to 1wt%. Hu et al. prepared boron containing carbon materials through the co-carbonization of 9-chloroborafluorene and pitch[47]. The authors proved that the boron content in the final product can be controlled, and they observed a significant effect of boron on graphitization at 2300°C. Boron loss was observed when boron doped carbon materials were heat treated at 2900°C[60]. Oxidation of the pressureless sintered microbead pellets in air was almost completely suppressed at 800°C with 10wt% B₄C doping [61]. The pellets were sintered in vacuum at 2000°C. The authors observed a significant increase in mechanical properties and a decrease in thermal conductivity with B₄C additions: flexural strength increased from 37MPa to 87MPa at 32.2 wt% boron addition.

There are several investigations on the properties of boride reinforced carbon composites. Hot-pressing was used in sample preparation in all cases. Tong et al. prepared ZrB₂/C composites from ZrO₂, B₄C, coal tar pitch and petroleum coke [62]. The mixture was hot pressed at 2600°C under 50MPa. The flexural strength of pellets with only ZrO₂ additions increased to 45MPa at ~10wt% loading from 25MPa, the flexural strength of pellets without additives. B₄C addition had a tremendous effect on the mechanical properties of the best composition, with flexural strength increasing to 130MPa at 2 wt.% B₄C addition. Pellets with only 2wt% B₄C addition have a flexural strength of 53MPa. The Zr/B atomic ratio is almost exactly equal to 0.5 with 3wt% B₄C addition. The authors measured the lowest porosity level (3.7%) for pellets with the optimum mechanical property. Unfortunately the extent of graphitization wasn’t
discussed in detail. Resistance of the composite materials to oxyacetylene flame ablation increased continuously with the increase in ZrB2 content [63]. Wen et al. prepared W2B5/C composites via an *in situ* reaction sintering route from B4C, WC and carbon black powder by hot pressing at 2000°C, 25MPa[64]. The W2B5 contents studied are in the range from 30-70 vol.%. Very dense materials were obtained with porosity levels less than 5.3%, and 100% relative density was achieved at 50 vol.% loading. Fracture toughness as determined by the Single Edge Notched Beam (SENB) method increased continuously with an increase in W2B5 content, from 3.28 MPa.m^{0.5} at 30vol% loading to 8.89 MPa.m^{0.5} at 70vol% loading. Only W2B5 and graphite phases were detected in the products. The authors observed a big increase in the extent of graphitization, but thought it was caused by the carbon black powders experiencing a much higher real temperature due to an exothermic reaction. Flexural strength, hardness, electric conductivity, and oxidation resistance improved dramatically as well[65]. Tribological behavior was investigated and the authors observed an increase in friction coefficient and a decrease in wear rate[66]. McKee found many borides such as AlB12, SiB4, ZrB2 and CrB2 improved the resistance of graphite to oxidation. The author attributed it to the inhibition effect of boron oxide[52].

The potential of boron containing compounds as oxidation inhibitors was investigated extensively in C/C composites. ZrB2 and B powder were added to the impregnation liquid at 15wt% loading by Ragan et al. to make the so called “matrix inhibited C/C composite” [67]. The composites were heat treated to temperatures ranging from 850°C to 2650°C. The additives significantly reduced the mechanical properties of the composites when heat treated above 2320°C with boron and 2330°C with ZrB2.
Microstructure analysis revealed marked fiber damage/crystallization. Composites with boron additions showed improved oxidation resistance. ZrB$_2$ was found to be less effective. The effect of boron additions on properties of C/C was studied systematically by Sogate et al.[68]. Boron carbide powder-impregnated carbon fiber felts were prepared by the slurry method and further densification was achieved using the CVI method. The composites were heat treated to temperatures ranging from 2000$^\circ$C to 2800$^\circ$C. The boron loadings studied are between 11-15wt%. Boron carbide distribution in the composites was proved to be homogenous by EPMA at a heat treatment temperature of 2400$^\circ$C or higher. Similarly, the authors observed fiber damage/crystallization at a heat treatment of 2400$^\circ$C or higher, which was accompanied by diminishing of anisotropy in coefficient of thermal expansion (CTE), increased graphitization and decreased binding strength. The oxidation rate decreased 22 times with boron carbide additions. Lee et al. on the other hand, found boron retention is higher in the order of phenolic resin, PAN-based fiber and pitch based fabrics when composites were heat treated at 2000$^\circ$C or 2400$^\circ$C[69]. It is not clear how they managed to provide boron concentration data with such high accuracy (~0.05wt%) using EPMA. McKee studied the effect of glass forming additives boron, silicon carbide and zirconium boride on the oxidation behavior of C/C[52]. All three additives were found effective in reducing the reactivity of the composite with air. However, spreading of the glass phase appeared to be slow and the inhibitors became effective only after appreciable fractions of carbon had been gasified. Ehrburger et al. found that at low boron loading, the decrease in oxidation rate is essentially due to blockage of active sites, while at higher boron oxide content, the formation of a mobile diffusion barrier for oxygen contributes significantly to the inhibition effect[70].
2.3.4. Noncarbide Forming Metals

Some metals, such as Co, Ni and Cu, do not form stable carbides. Cu in general doesn’t react with carbon at all, while Ni and Co have long proved to be effective catalysts for graphitization[53, 71]. The temperature at which catalytic graphitization occurs depends on the precursor material[72] and structure of the product was found determined primarily by the size of the metal particles[73]. For graphitizable precursors, addition of large nickel particles (>50nm[10]) leads to the formation of a G (graphitic)-component, while only a turbostratic component was discovered for samples prepared via an organic metal precursor (nickelocene) impregnation method. For samples with large nickel particle additions, the size of the nickel particles decreases as they diffuse into the carbon matrix and result in the formation of a turbostratic component[10]. The mechanism of G-component formation is generally believed to be of a dissolution-precipitation type similar to the catalytic graphitization by carbides. Two mechanisms were proposed to explain the formation of the turbostratic component. The first mechanism is similar to the formation of the G-component. However, as the size of the particles is much smaller, a T-component is obtained instead. In the second mechanism, it is believed that the carbon precursor materials consist of turbostratic elementary domains and domain boundaries which won’t grow during heat treatment. Metal particles react preferentially with boundary carbon and the turbostratic elementary domains coalesce to grow on the metal surface. No structural memory of the parent carbon will remain in the T-component if the graphitization follows the first mechanism which is contrary to the result of some authors[10].
Ti/Ni and Fe/Ni binary alloys were used by Hu et al. as reinforcement for carbon pellets based on MCMBs[74]. The alloy additives are unique as eutectic liquid forms below the heat treatment temperature (1400°C). Samples were prepared by tape-casting, molding at 150MPa, 85°C and vacuum sintering. A very high extent of graphitization was achieved at high loadings as the $d_{002}$ spacing approached that of natural graphite and large graphite crystals were observed on the fractured surface. The bending strength of the product increased with an increase in Ti/Ni loading up to 60wt%. For pellets with Fe/Ni additions, bending strength increased initially with an increase in loading up to 30wt% loading, and then decreased. The relative density of the product was rather low, being less than 80% for most samples with the best one at 87.8%.

2.4. Fracture Toughness Testing

As mentioned in the first chapter, the biggest challenge for this project is the improvement in fracture property. In this section, fracture toughness testing methods and their application in the field of carbon graphitic materials will be presented. Fracture toughness is a measure of the materials’ ability to resist the growth of a pre-existing crack or flaw. There are 3 fundamental modes of fracturing: opening (mode I), shearing (mode II) and tearing (mode III). The plane strain fracture toughness ($K_{IC}$) is a fundamental materials property. In order to have a valid “plane strain” state, the thickness of the test specimen has to satisfy the following condition:

$$B \geq 2.5 \left( \frac{K_{IC}}{\sigma_y} \right)^2$$
Where $\sigma_y$ is the 0.002 strain offset yield strength of the material [63]. Based on literature study, the yield strength for carbon pellets sintered from mesocarbon microbeads is around 100Mpa. If we assume the fracture toughness value is less than $2\text{Mpa.m}^{0.5}$, then a valid plane strain fracture toughness measurement requires that the thickness of the sample be greater than 1mm.

![Diagram](image)

(a) 

(b) 

(c) 

(d) 

Figure 2.2: Specimen configurations for (a): SENB and (b-d): compact tension fracture toughness tests

At present there is no standard specifically designed for fracture toughness measurement of brittle materials such as carbon. All ASTM standards were originally developed for the measurement of metallic specimens.
Single edge notched beam (SENB) and compact tension (CT) specimens are the two most commonly used test configurations. The SENB sample is similar to that used in the bending test, as shown in Fig. 2.3(a). Depending on practical considerations, compact specimens, arc-shaped specimens or disc-shaped compact specimens, as shown in Fig. 2.3 (b-d), are tested for determination of fracture toughness.

The fracture measurements are based on the theory of linear elastic fracture mechanics (LEFM), in which an ideal planar crack with a zero root radius is assumed. Natural cracks such as fatigue cracks are the sharpest cracks that can be produced in the laboratory; however, because of the very limited extent of plastic deformation at the notch tip of brittle materials, the metallurgical cyclic fatigue technique is impractical for ceramic materials such as carbon[75]. In the study of graphitic materials, in general only an initial notch of 100-300 microns was cut using a diamond saw. The resultant radius of notch tip was claimed to be less than 10 microns[76-78]. No effort on creation of fatigue cracks was reported in literature. The fracture toughness value measured from those practices could be a little higher than $K_{lc}$ of the materials.

![Figure 2.3: Specimen configurations for Chevron-notch fracture toughness test](image)
Chevron-notch fracture toughness testing was designed to solve this problem. Both rod specimens of a circular cross section and the rectangular bar specimens, as shown in fig. 2.4, could be used in the measurement. The crack initiates at a low force at the tip, and each incremental increase in crack front width requires further increase in force. Steady state crack propagation is assumed before reaching the maximum load. As the maximum load required for the fracture toughness calculation was reached in the progress of crack propagation, a fatigue pre-crack is no longer necessary. However, the fracture toughness value may differ from what obtained from other test methods. The main advantages include the ability to test very small samples, low equipment requirements, etc. Unfortunately, at present it is more convenient for us to prepare thin pellets, not ideal for machining to a rod or bar specimen that has a circular or square cross section. Moreover, the machining process takes more than one day, 5-10 times higher than what takes to machine a disc shaped compact tension specimen.

Other methods for the evaluation of fracture properties include Charpy and Izod tests, double cantilever beam (DCB) test, indentation test, etc. However, they were never adopted as ASTM standards. Charpy and Izod tests are purely qualitative in nature and they don’t determine fracture toughness. The DCB test also requires a fatigue pre-crack which is impossible for brittle ceramics. The indentation test however, is ideally suited for toughness evaluation on a comparative basis[79], and previous studies found fairly good correlation between the value obtained from an indentation test and conventional tests[80]. The major advantages of the test also include the ease of sample preparation, as a polished surface is all that is needed. Moreover, in general a Vickers hardness tester is good enough for the experiment. To make a valid test, the length of crack extension
should be greater than the size of the indenter. Regarding the application of the technique in carbon graphitic materials, we found it is quite difficult to generate a valid crack. No extension cracks were observed under polarized light when heat treated pellets were subject to a 1Kg load in a Vickers hardness tester. We also tested the pellets heat treated at 2400°C at the Honeywell facility in South Bend using a Rockwell hardness tester, which according to Honeywell engineers, has a pyramid shaped indenter. No extension crack was observed at a 15Kg load and the crack length is still less than the dimension of the indenter at a 30Kg load. The only application in carbon graphitic materials was carried out by Garcia-Rosales et al.[45]. Unfortunately, the experimental conditions were not described in detail. The fracture toughness values obtained by indentation were found to be significantly higher than that obtained from a bending test and only a limited number of fracture toughness values were presented.

In situ observation of the damage initiation in notched graphite samples was made by Salazar et al.[78]. The experiments indicate that for coarse grained graphite, damage progressed by the linkup of the cracks and failure occurred after certain amount of stable crack growth, while for fine grained graphite, damage was localized at the notch root. Relatively high stress is required to nucleate a crack, and it then grew unstably leading to immediate specimen failure.
CHAPTER 3:
EXPERIMENTAL

The characteristics of the materials used and details of the techniques applied in sample processing and characterization will be described in this chapter.

3.1. Materials

The MCMB-6G mesocarbon microbeads were provided by Osaka Gas, Japan. They were manufactured from coal-tar pitch and have an average particle size of 7.62 μm. Characteristics of the batch of microbeads used are summarized in Table 3.1. Properties of the various reinforcements are listed in Table 3.2.

| TABLE 3.1 |
| CHARACTERISTICS OF MESOCARBON MICROBEADS |
|---|---|
| Particle Size | 10 % < 0.72 μm |
| | 50 % < 7.62 μm |
| | 90 % < 17.01 μm |
| Toluene Insoluble | 94.8 wt % |
| Quinoline Insoluble | 89.9 wt % |
| β-Resin | 4.9 wt % |
TABLE 3.2
CHARACTERISTICS OF REINFORCEMENTS

<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Stock number</th>
<th>Important properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milled carbon fiber</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonflex carbon fiber, P-100</td>
<td>Anshan East Asia Carbon Fiber Company, Ltd.</td>
<td>Lot No. 990972</td>
<td>Pure carbon, PAN fiber DIAMETER: 13.4µm LENGTH: 75µm-150µm</td>
</tr>
<tr>
<td>Donacarbon S series</td>
<td>Donac Co., Ltd.</td>
<td>-</td>
<td>Thermosetting fiber, carbon &gt;95%, pitch based DIAMETER: &lt;13µm LENGTH: 110µm-370µm</td>
</tr>
<tr>
<td>B</td>
<td>Alfa Aesar</td>
<td>39680</td>
<td>APS &lt;5µm, 94-96%</td>
</tr>
<tr>
<td>B₄C</td>
<td>Industrial supply</td>
<td>120202</td>
<td>0.75µm</td>
</tr>
<tr>
<td>TiB₂</td>
<td>Alfa Aesar, Acros Organics</td>
<td>44558</td>
<td>325 mesh, 99.5%</td>
</tr>
<tr>
<td>TiB₂</td>
<td>Alfa Aesar, Acros Organics</td>
<td>336289</td>
<td>325 mesh, 99.5%</td>
</tr>
<tr>
<td>Ti</td>
<td>Alfa Aesar</td>
<td>42624</td>
<td>325 mesh, 99.5%</td>
</tr>
<tr>
<td>TiC</td>
<td>Alfa Aesar</td>
<td>40178</td>
<td>325 mesh, 99.5%</td>
</tr>
<tr>
<td>TiN</td>
<td>Alfa Aesar</td>
<td>41556</td>
<td>325 mesh</td>
</tr>
<tr>
<td>ZrB₂</td>
<td>Cerac</td>
<td>Z-1031</td>
<td>325 mesh, typically &lt;10µm, 99.5%</td>
</tr>
<tr>
<td>Al</td>
<td>Sigma-Aldrich</td>
<td>266515</td>
<td>20 µm 99+%</td>
</tr>
<tr>
<td>Cu</td>
<td>Aesar</td>
<td>101588</td>
<td>325 mesh, 99.3%</td>
</tr>
<tr>
<td>Ni</td>
<td>Cerac</td>
<td>N-1089</td>
<td>APS 5µm, 99.9%</td>
</tr>
<tr>
<td>Nickel acetylacetonate hydrate</td>
<td>Avocado Research Chemical Ltd.</td>
<td>15148</td>
<td>95%</td>
</tr>
</tbody>
</table>

3.2. Processing

3.2.1. Oxidation Pretreatment

To study the effect of oxidation on shrinkage behavior and properties of sintered carbon pellets, part of the microbeads were oxidized in pure oxygen or air prior to any
heat treatment. The microbeads were oxidized in situ in thermal analysis experiments to monitor the weight variation. The preparation of samples for X-ray diffraction, dilatometry and mass spectrometry characterization were carried out under oxygen flow in a tube furnace. The microbeads were heated to the designated temperature at a heating rate of 1 degree per minute and held for 1hr. For mechanical testing, since a larger quantity of sample is required, microbeads were oxidized in air at the designated temperature for 8hrs, with a 1 degree per minute heating rate again being used.

3.2.2. Preparation of Green Pellet and the Heat Treatment Procedure

The microbeads and reinforcement powders were mixed homogeneously in a mechanical mixer (Spex 8000) and compressed uniaxially (Carver Autoweries) into 31nm green pellets at the designated pressures. In most cases, the compact pressure is 100MPa.

Carbonization and graphitization were carried out in a graphite furnace (Astro 1000-2560-FP20) in one step. The graphite furnace has a hot zone which is 2 inches in diameter and 6 inches in height. Temperature control was achieved by a thermocouple at temperatures below 1000°C and by optical pyrometer at higher temperatures. The furnace was operated under a helium overpressure of 5-10 psi. The heating rate was 1K/min at temperatures lower than 1800K and 10K/min afterwards. The pellets were graphitized at the designated temperature for 2hrs in all cases. The content, in general, represents the volumetric concentration of reinforcement in the final form in the heat treated pellets.
3.3. Characterization

3.3.1. Thermal Analysis

Thermal analysis was performed in a simultaneous TGA-DTA instrument (TA Instruments 2960). Oxygen free argon (99.996%), with an oxygen concentration less than 0.5ppm was used as the carrier gas at a flow rate of 100ml/min. The microbeads were oxidized in situ using pure oxygen (99.99%) with a heating rate of one degree per minute. After oxidation, the carrier gas was switched automatically to argon and a heating rate of 5 degrees per minute was used in the subsequent carbonization after flushing for 4 hours.

3.3.2. Thermogravimetry-mass Spectroscopy

TG-MS was used to characterize the gas product evolved during low temperature heat treatment. The weight variation was monitored using a TGA (Hi-Res Modulated TGA, TA Instruments 2950). At the same time, composition of the exhaust gas produced during thermal analysis was analyzed using a quadrupole mass spectrometer (QMS Series Gas Analyzer, Stanford Research Systems). A specially designed filter, filled with glass wool, was used to trap the high molecular weight fractions and prevent blocking of the capillary caused by condensation. Oxygen free argon was used as the carrier gas at a flow rate of 50ml/min. About 100mg of sample was used in the analysis, and a 20 degree per minute heating rate was applied to increase the intensity of the signal.

3.3.3. X-ray Diffraction

Phase composition and crystal parameters (interlayer spacing, d_{002}, and crystallite size, L_c) were analyzed using an X-ray powder diffractometer (Scintag X1 Thermo Corp.,
Waltham, MA). Samples were crushed into fine powders prior to analysis. Silicon powder was added for use as an internal reference. Crystallite size was calculated based on Scherrer’s equation and the constant was set at 0.89. Some authors claimed that the lattice parameters measured using this technique may differ from the real value due to defects in the turbostratic carbon[81] especially when crystallite size is below 3nm[82]. Unfortunately there is no easy alternative available at this stage. Nonetheless, this simple technique is still good for a comparative basis; moreover, the accuracy is good for particles with higher local order such as the heat treated microbeads.

3.3.4. Dilatometry

Linear shrinkage was characterized by using a Linseis Dual Sample Horizontal Dilatometer (Model L75HD1550). Specimens for the dilatometry experiments were prepared by compressing about 150mg of sample powders in a 5mm die under 450MPa. The instrument was calibrated using a polycrystalline alumina reference that allows an accuracy of 10nm at temperatures up to 1500°C. Experiments were conducted in argon or nitrogen at a flow rate of 240ml/min.

3.3.5. Particle Size and Zeta Potential

Acoustic techniques (DT-1200, Dispersion Technology Inc.) were used to simultaneously determine the particle size and zeta potential. Mesocarbon microbeads were dispersed in 70wt% isopropanol-water mixture to make the 5wt% solid-containing slurry for the measurement. pH of the mixture was increased by adding 1M sodium
hydroxide solution. After pH reached about 12, 1M hydrochloric acid was used to decrease the pH until about 3.

3.3.6. Microstructure

The heat-treated pellets were polished for examination by conventional metallographic techniques. The polished cross sections were observed under polarized light (Olympus BX-61). The fresh surface after fracture testing was studied with an SEM (Model Envo6, Oxford Instruments, Eynsham, UK) equipped with an EDS detector (INCA Microanalysis system, Oxford Instruments).

3.3.7. Laser ablation ICP-MS

Quantitative analysis of boron concentration in the carbon matrix was measured using a laser ablation ICP-MS. Laser ablation was performed with a New Wave UP 213 UV (213 nm) frequency quintupled Nd:YAG pulsed laser. The laser was operated with a repetition rate of 10 Hz and energy density 7 J.cm$^{-2}$ for raster analyses using a 30 micron laser beam, and at 4 Hz and 10 J.cm$^{-2}$ for spot analyses with a 15 micron laser beam. Ablated material was delivered in a He carrier gas to a Thermo-Finnigan Element 2 double focusing magnetic sector high resolution ICP-MS. The ICP-MS was operated in medium resolution, fast magnet scanning mode, and one point per peak was measured following the protocol of Longerich et al. [83]. All data were collected in a time resolved mode, and the total sweep time for the selected range of isotopes ($^{11}$B, $^{12}$C, and $^{47}$Ti) was 211 milliseconds. Four sweeps were combined into one reading to minimize noise associated with the transient laser ablation signal. Data were reduced following the
methods of Longerich et al. [83] minus the application of a volume correction due to the identical matrices of our samples and the calibration standard.

3.3.8. Oxidation

The isothermal oxidation loss of the pellets in air was measured using a Hi-Res Modulated TGA (TA Instruments 2950). Rectangular specimens, with nominal dimensions of $4 \times 1 \times 10 \text{mm}^3$ were cut from the heat treated pellet using a diamond saw and suspended on top of the sample pan using a platinum wire in order to expose all surfaces to the ambient. After flushing for 2hrs, the specimen was heated in nitrogen flow to $800^\circ\text{C}$, and then dry air was introduced at a flow rate of 200ml/min.

3.3.9. Pore Size Distribution

Open porosity and pore size distribution of the heat treated pellets were analyzed in a commercial lab (Micromeritics Analytical Services) using a mercury porosimeter (AutoPore IV 9500). About 2-3 gram of specimen was used in the experiment. An intrusion test was performed to determine total open porosity, the distribution of pores between 360 and 0.003 $\mu\text{m}$ in diameter, bulk density, skeletal density, etc.

3.3.10. Fracture Testing

Fracture toughness of the pellets was measured using ASTM E1820-01 as a guideline. The samples were machined using electron discharge machining (EDM). The configuration of the machined pellet is shown in Fig 3.1. The pellets were fractured in tension (Applied Test Systems, ATS 900) with a crosshead speed of 0.13 mm/min. The
extension of the sample during testing was monitored using an extensometer (MTS 632.12E-20).

Figure 3.1: Schematic of disc shaped pellets machined for fracture toughness testing. The width of the of crack initiation notch, $d$, is 300 microns. $W$ and $a$ were fixed at 20mm and 9mm respectively.

The fracture toughness was calculated as

$$K = \frac{P}{(B^2W)^{3/2}} f\left(\frac{a}{W}\right)$$

$$f\left(\frac{a}{W}\right) = \frac{\left(2 + \frac{a}{W}\right) \left(0.76 + 4.8\left(\frac{a}{W}\right) - 11.58\left(\frac{a}{W}\right)^2 + \right)}{\left(1 - \frac{a}{W}\right)^{3/2}}$$

Where $K$ is the fracture toughness, $P$ is the load at fracture and $B$ is the sample thickness. Five samples were prepared and tested for each composition and the average value is taken as the fracture toughness of the material.
CHAPTER 4:
EFFECT OF OXIDATION ON CARBONIZATION BEHAVIOR AND
PROPERTY OF THE SINTERED CARBON PELLETS

In this chapter, we attempt to develop a better understanding of the carbonization behavior of our carbon precursor material, mesocarbon microbeads, which is critical to the development of materials properties. This was achieved by characterizing the weight loss, gas product composition, shrinkage behavior, development of crystal structure and microstructure, etc. The other objective is to explore the full potential in terms of fracture property of the mesocarbon microbeads, by optimizing the processing conditions and by pretreatment such as oxidization. Pretreatment in air or oxygen is a rather common practice in the carbon industry. It is an important step in the manufacturing of PAN and pitch fibers[1] and also was used to adjust the plasticity of mesophase pitch[34] before the sintering practice. In addition, as many of the processing steps including storage, mixing, compressing, drying (if slurry practice was used), etc, of the microbeads were conveniently conducted in air, it is interesting to see how oxidation may affect the sintering process and mechanical properties. For this purpose, the microbeads were pre-oxidized in oxygen. The carbonization behavior was characterized and the results are compared with that of original microbeads. Some microbeads were oxidized in air and graphitized to evaluate the fracture property due to the large quantities required for mechanical testing.
4.1. Results and Discussions

4.1.1. Thermal Analysis

The weight variations of microbeads during oxidation along with the temperature excursions used are shown in Fig 4.1. For each temperature studied, the experiment was performed under both oxygen and oxygen free argon flow. Comparison of the weight variations of microbeads demonstrates the effect of oxidation on the weight change of the microbeads. When the pretreatment temperature is 100°C, the microbeads weight change follows roughly the same trend in both flows (oxygen and argon). At a 150°C oxidation temperature, the weight loss of microbeads in an inert gas flow is higher than in the oxygen flow, indicating the occurrence of chemical reactions between oxygen and microbeads. The difference between weight variations in the two gas streams increases

Figure 4.1: Weight variation of microbeads during thermal analysis in oxygen (O₂ series) and argon flow (Ar series) along with temperature excursions
with an increase in the oxidation temperature. At 300°C during the oxidation pretreatment, the weight of microbeads increased initially but then about 0.4% weight loss was observed during the isothermal process. The TGA results indicate that the oxidation process is a competition between weight gain and weight loss. Oxidation introduces some oxygen into the structure and leads to the weight increase. At the same time, chemical reactions can consume some carbon and hydrogen, which are released as water vapor and carbon-oxygen gases, leading to a weight loss. At low temperature, the overall effect is a weight increase. However, when the pretreatment temperature is 300°C or higher, more carbon and hydrogen are consumed due to increased reactivity and the weight loss prevails.

After oxidation pretreatment, the carrier gas was automatically switched to oxygen free argon. The derivative of weight change as a function of temperature with

![Graph showing DTG profile](image)

**Figure 4.2:** DTG profile of (a) original and microbeads oxidized at (b) 100°C, (c) 150°C, (d) 200°C, (e) 250°C and (f) 300°C.
further heating in the Ar environment is shown in Fig 4.2. The volatile materials were released from original microbeads in three decomposition steps, with peak temperatures located at 225°C, 519°C and 751°C respectively. The oxidation pretreatment at 100°C didn’t change the differential thermogram (DTG) profiles relative to the untreated sample, giving further evidence that the oxidation reaction is not very important at this temperature. For microbeads oxidized at 150°C, the peak temperature (originally 225°C) of the first decomposition process increases due to the release of volatile material during oxidation pretreatment. The intensity of the second decomposition peak decreases significantly, although its peak temperature (519°C) remains unchanged from that of the original microbeads. At higher oxidation temperatures, the peak temperature of the first peak increases further with the increase in pretreatment temperature. The peak temperature of the second decomposition process however, moved to 586°C. This decomposition step dominates the weight loss for microbeads oxidized at 300°C. The peak temperature of the third decomposition process remains unchanged after oxidation.

The yield, defined by the material left after heating the microbeads to 900°C during thermal analysis (oxidation and carbonization) divided by the original microbead mass, is nearly the same (difference less than 0.4%) for original microbeads, and microbeads oxidized at 100°C, 150°C and 200°C. This result indicates that the fraction of microbeads that reacted with oxygen in these temperature regions is exactly what will be released during carbonization of pure microbeads. In general, oxidation was found to increase the carbon yield[35]. This discrepancy may be explained by the following three reasons. First, in the TGA experiment, very fine powder was used, so the gas product was quickly released without further polymerization reaction. As will be shown in the
mechanical testing, when microbeads were compacted into pellets, the carbon yield increased by 1.4% if microbeads were oxidized at 150°C (Table 4.1). Secondly, the microbeads we used have a very high carbon yield (~90%, 900°C). Finally, the fraction oxidized at temperatures less than 200°C has a rather simple structure, so the oxidation products are less likely to have residue left in the carbonized product. When microbeads are oxidized at higher temperature (250°C, 300°C) the yield decreases, an indication that the mesophase itself has been oxidized.

4.1.2. *Thermogravimetry-mass Spectroscopy*

The gas products generated during heat treatment give important information on the chemical reactions that are occurring. Drbohlav et al. [31] separated the gas released during thermogravimetric analysis into 4 different fractions, based on their difference in liquidation temperature and absorption property on molecular sieve. After separation, the composition of each fraction was studied by sub-ambient distillation and subsequently characterized using FTIR. Although a full description of the gas composition was revealed, since a complete separation of the materials was not achieved in the very first step, it is difficult to discuss the details of the pyrolysis reactions.

In this work, the composition of the gas released during thermal analysis of mesocarbon microbeads is characterized *in situ* using mass spectroscopy. In order to achieve real time results, a thermal analyzer equipped with a small heating chamber is used. Initial experiments revealed that the gas product has a very complicated composition. In this research, we targeted at the analysis of small molecules, such as methane, carbon oxides and hydrogen. The remaining part of the off-gas, which is
Figure 4.3: TG-MS characterization. (a) MS profile of gas released from original microbeads during carbonization, (b) MS profile of gas released from microbeads pre-oxidized at 250°C for 1 hour in oxygen, (c) Comparison of differential weight variation of original microbeads with weight loss caused by hydrogen release. The DTG profile was deconvoluted using Lorentz multi-peak fitting method into 3 peaks, with the third peak corresponding to hydrogen release, (d) Comparison of weight loss of microbeads oxidized at 250°C with carbon monoxide MS profile. The second peak corresponds to the release of carbon monoxide.

composed of rather high melting point components, is captured by a glass wool trap to prevent blockage of the gas sampling capillary.

As demonstrated in Fig 4.3(a), methane and hydrogen are detected during carbonization of pure microbeads. Methane was released at temperatures between 500-800°C. The signal of hydrogen and argon are two orders of magnitude higher than the other components. As a result, the gas sampled by the mass spectroscopy can be
regarded as composed of hydrogen and argon only. If we make the assumption that the total pressure at inlet is a constant, 1 atm, then the relative sensitivity of hydrogen to argon can be calculated as

\[ S_{H_2, Ar} = \frac{Ar_{(baseline)} - Ar_{(minimum)}}{H_{2(maximum)} - H_{2(baseline)}} \]

Since the flow rate of argon is constant, 50 ml/min, the weight loss due to hydrogen generation can be calculated as

\[ W_{H_2} = \frac{H_{2(MS)} \times S_{H_2, Ar} \times 50 ml/min \times 1 atm}{Ar_{(baseline)} \times RT(300 K)} \times 2 \]

The weight variation of microbeads during carbonization was also monitored and the derivative weight loss profile shows three maxima, which are located at 273°C, 540°C and 782°C respectively [Fig 4.3(c)]. The Lorentz multi-peak fitting method was used to divide the differential weight loss curve into three separate peaks that are shown by the dashed lines. The weight loss due to hydrogen release, as shown in Fig 4.3(c), has roughly the same peak temperature and magnitude as that of the third decomposition process. It is thus concluded that the third weight loss event is mainly caused by the release of hydrogen. Based on this calculation, we found that dehydrogenation accounts for 2.5% weight loss.

Although dehydrogenation only accounts for a rather small weight loss, the chemical process associated with it could make major contribution to the volume shrinkage. Norfolk et al. [8] demonstrated that the process associated with the third peak in the weight loss profile is responsible for the shrinkage. Here we find this weight loss is caused by dehydrogenation. The derivative shrinkage of microbeads has a maximum at
732°C. The maximum hydrogen release, however, happened at 793°C, as shown in Fig 4.3(a). Further investigation revealed that this is caused by the different heating rate used in these two experiments. The high molecular weight materials, which account for most of the weight loss, are released at lower temperature. The release of those high molecular weight materials will not make a significant contribution to the shrinkage behavior since most of those materials are released before the major shrinkage event.

The same experiment was also performed on microbeads oxidized at 250°C. As shown in Fig 4.3(b), besides hydrogen and methane, carbon-oxides were also detected. The initiation temperature of methane release shifts from around 500°C to about 600°C, while the temperature of maximum hydrogen release is not affected by oxidation pretreatment. The maximum carbon monoxide release happened at 612°C (MS profile), the same as the peak temperature of the second decomposition process (TG profile) as shown in Fig 4.3(d). Apparently, the characteristic decomposition process of microbeads oxidized at 250°C or higher, with peak temperature located at 586°C as seen in Fig 4.2, is due to the release of carbon monoxide.

Although oxygen free argon is used as the carrier gas, a gradual increase in carbon monoxide signal is still observed in Fig 4.3(a, b), indicating the existence of oxygen. This could be caused either by residual oxygen left after flushing or an air leak into the reaction chamber. The experimental results in general should not be affected since carbon monoxide produced in this way is very small.
4.1.3. **X-ray Characterization**

During heat treatment of pitch, the polynuclear aromatic molecules or mesogens stack in parallel to form a discotic nematic liquid crystal system, which is the origin of mesophase carbon as first discovered by Brooks and Taylor [3]. During carbonization,

![Graph](image)

**Figure 4.4:** Variation of (a) crystallite size and (b) d\textsubscript{002} spacing of as-received and 200°C oxidized microbeads with heat treatment temperature.

this localized order is subject to change because of structure variations caused by pyrolysis reactions. X-ray diffraction gives the average size and interlayer spacing of this localized order and has been used by Haridoss et al. to characterize the structure change during carbonization of microbeads [27]. Here we used the same technique to monitor the effect of oxidation. For unoxidized microbeads, the crystallite size reached a maximum at 450°C [Fig 4.4(a)], and then decreased with an increase in heat treatment temperature until about 750°C. This increase in disorder is likely caused by the gas evolved due to pyrolysis reactions, with the most significant contribution coming from dehydrogenation. The initiation of this process, at a temperature just below 500°C, agrees fairly well with the initiation temperature for hydrogen release as detected by mass spectroscopy. At temperatures above 800°C, the chemical process that leads to hydrogen release is about to
terminate and the order is regained. As a result, the $d_{002}$ spacing [Fig 4.4(b)] decreases and crystallite size increases with an increase in heat treatment temperature. The crystallite size increases further at higher temperatures due to the solid state sintering process.

Oxidation pretreatment doesn’t have much impact on the crystallite size and $d_{002}$ spacing of microbeads. This fact indicates that the stacked chains that show regularity during x-ray analysis were not affected by oxidation pretreatment at 200°C. The crystallite size of pure microbeads increases around 450°C, while for oxidized microbeads this increase in local order disappears, and the crystallite size decreases continuously with the increase in heat treatment temperature. The variation of $d_{002}$ spacing as a function of temperature follows roughly the same trend for both the original microbeads and microbeads oxidized at 200°C, as shown in Fig 4.4(b).

In order to understand the loss of the increased local order of oxidized microbeads, recall that the mesophase is created at a temperature between 350-500°C. In this temperature region, if favorable conditions are provided, (e.g. being heat-treated at temperatures higher than the synthesis temperature), this localized order will increase just like when they were generated. It is believed that liquid phase sintering is the controlling mechanism in this temperature region. In this scenario, part of the mesophase microbeads (mainly beta resin), transforms into liquid, creating an environment very similar to what the microbeads experienced during their generation. Similar to mesophase pitch, oxidation decreases the plasticity of microbeads and consequently the liquid phase doesn’t form. As a result, the increase in local order by rearrangement of mesogens within the microbeads is impeded. The finding by Meada et al. that oxidation suppresses
the growth of mesophase from isotropic pitch agrees with our experimental results [84] [85].

4.1.4. Zeta Potential and Particle Size Measurement

Zeta potential and particle size were measured simultaneously using DT-1200 and the results are shown in Fig 4.5. The pH of a pure microbeads/70wt% isopropanol-water slurry is 7.7. It decreases to 5.8 after microbeads are pre-oxidized at 200°C. The isoelectric point (IEP) of the slurry also decreased from 9 to 5. This result proves that some acidic functional groups are produced during the oxidation pretreatment. It is interesting that the zeta potential of the oxidized microbeads is relatively high if the pH of the slurry is above 9, a condition readily available by adding ammonium hydroxide. Particle size analysis didn’t give a bimodal distribution but the average particle size is very close to the data provided by the manufacturer and as supported by SEM analysis.

![Figure 4.5: Zeta potential as a function of PH of (a) original microbeads, (b) microbeads heat treated at 200°C, 1hr in oxygen](image)

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4.1.5. *Shrinkage of Green Pellets during Carbonization*

The green density of the pellets made from original microbeads increased continuously with compaction pressure up to 180Mpa. After carbonization and graphitization at 2400°C for 2hrs, only the pellets compacted at or under 100Mpa survived (Fig 4.6). For pellets compacted at higher pressures, the appearance of cracks and corrugations on the surface indicated that defects were formed during carbonization. Pellets with a final density as high as 1.94g/cm³ were obtained after graphitization.

![Graph showing bulk density of green and graphitized pellets made from original microbeads.](image)

**Figure 4.6:** Bulk density of green and graphitized pellets made from original microbeads. Samples that failed during carbonization as evidenced by the appearance of surface cracks are indicated with ‘x’.

In order to understand the mechanism of crack formation, the original and oxidized microbeads were compacted at 450Mpa and a dilatometer was used to characterize the linear shrinkage. The effect of oxidation on crack formation is shown in Fig 4.7. When microbeads were oxidized at 150°C or higher, a smooth, gradual variation
Figure 4.7: Linear shrinkage of pellets made from (1) original and microbeads oxidized at (2) 100°C, (3) 150°C, (4) 200°C, (5) 250°C for 1 hour in oxygen. A sharp swelling peak appears at temperature around 485°C on curve 1 and 2.

in sample length at temperatures between 420°C and 500°C was observed, due to release of compression stress and sintering. However, for pellets made from original microbeads and microbeads oxidized at 100°C, a sharp swelling peak was found in the same temperature region. Detailed experiments showed that this swelling event is responsible for the crack formation. In addition it was found that the extent of swelling decreased with increasing oxidation temperature.

The samples from the dilatometer experiment were polished and their microstructures were studied by optical microscopy. As shown in Fig 4.8(a), large cracks were seen in the polished cross section of pellets compacted from original microbeads. After oxidation pretreatment at 100°C for 1hr, the size of the cracks decreases significantly, but still causes the swelling observed in the dilatometer experiments [Fig
4.8(b)]. These cracks will significantly decrease the mechanical properties. For microbeads oxidized at 150°C or higher, a uniform structure with homogeneously distributed pores was seen after carbonization [Fig 4.8(c)]. The size and total volume of the pores increase significantly when the oxidation temperature is above 200°C [Fig 4.8(d)].

The apparent viscosity of a coal tar pitch-based mesophase powder, as studied by Hoffmann et al., has a minimum at temperatures between 420-490°C [22]. The properties of their mesophase powder (100% optical anisotropy, 97% toluene insoluble fraction and 92.6% quinoline insoluble fraction) are very similar to the microbeads used here. Because

Figure 4.8: Optical micrographs of polished cross sections of samples taken after dilatometer testing up to 1500°C in argon: (a) microbeads as received and microbeads preoxidized at (b) 100°C, (c) 150°C and (d) 250°C for 1hr in oxygen.

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of these similarities, we believe that our microbeads will also have minimum viscosity in the same temperature region. The temperature of crack formation lies in the same temperature region where microbeads have the lowest viscosity. This is the temperature region where the light components, mainly beta resin, transform into a highly viscous liquid. Under the influence of capillary force, this liquid is transported to fill the narrowest openings. The gas generated by thermal decomposition thus has no way to escape, resulting in pressure increases and crack formation. This is corroborated by the microstructure study. In Fig 4.8(a), large cracks were found around the center of the pellet. Based on the above reasoning, it is suggested that a gas impermeable condition is formed when microbeads are heated treated to temperatures around 485°C. The cracks are formed because the gas generated during heat treatment cannot escape.

The oxidized microbeads have much lower plasticity, similar to oxidized mesophase pitch. As a result, a gas impermeable condition never develops during heat treatment and thus crack formation is suppressed. At temperatures higher than 200°C, the oxidation of mesophase leads to increased weight loss and as a result, apparent density decreases and porosity increases after heat treatment.

4.1.6. Mechanical Testing

Oxidation pretreatment is an essential step when mesophase pitch is used as raw material in the production of carbon products. However, high-density carbon components can be made using mesocarbon microbeads without oxidative stabilization. In the dilatometer experiments we found that high-density carbon materials can also be made from oxidized microbeads. It is thus interesting to see whether mechanical properties
benefit from oxidation pretreatment. For this purpose microbeads were oxidized in air at different temperatures, and then compacted uniaxially into disc-shaped green pellets. The bulk density of both the green pellet and graphitized product increased with an increase in compact pressure, as shown in Figure 4.9. For comparison, all pellets made from oxidized microbeads were compacted at 300MPa for fracture toughness testing. After carbonization, cracks were found on pellets made from microbeads oxidized at 100°C and 125°C. Pellets made from microbeads oxidized at higher temperatures survived without crack development. The properties of pellets, green and graphitized, are listed in Table 4.1. The oxidation pretreatment does not affect the extent of graphitization, since d_{002} of the graphitized pellets are almost the same. This is due to the fact that most oxygen is released as carbon oxides well below the temperature where thermally activated
<table>
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<tr>
<th>Materials</th>
<th>Compaction Pressure (Mpa)</th>
<th>Green Density (g/cm³)</th>
<th>Volume Shrinkage (%)</th>
<th>Weight Loss (%)</th>
<th>Final Density (g/cm³)</th>
<th>D₀₀₂ (nm)</th>
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<td>12.6</td>
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<td>1.94</td>
<td>0.3378</td>
</tr>
<tr>
<td>Mcmb, 175°C 8hrs air</td>
<td>300</td>
<td>1.40</td>
<td>36.7</td>
<td>12.2</td>
<td>1.94</td>
<td>0.3380</td>
</tr>
<tr>
<td>Mcmb, 200°C 8hrs air</td>
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<td>36.9</td>
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<td>1.93</td>
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<td>1.41</td>
<td>37.3</td>
<td>15.8</td>
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</tr>
<tr>
<td>Mcmb, 250°C 8hrs air</td>
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<td>36.9</td>
<td>17.6</td>
<td>1.79</td>
<td>0.3377</td>
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</tbody>
</table>

Graphitization takes effect. Graphitized pellets with the same bulk density, 1.94g/cm³, were made from both original microbeads and microbeads oxidized at 150°C and 175°C. The density of green pellets made from original microbeads was much lower, since they were compacted at much lower pressure. However, they shrank more during heat treatment, resulting in graphitized pellets with the same bulk density as those made from oxidized microbeads that were compacted at higher pressure. Pellets made from microbeads oxidized at temperatures higher than 200°C suffered from larger weight loss and as a result the final density was lower after heat treatment.

The fracture toughness of the graphitized pellets, as measured by compact tension test, is shown in Fig 4.10. The pellets made from original microbeads gave the highest resistance to fracture propagation. Even though the bulk density of the pellets made from original microbeads and microbeads oxidized at 150°C and 175°C are about the same, the fracture toughness decreased slowly with the increase in oxidation temperature. This indicates that oxidation pretreatment is ineffective when high fracture property is desired.
Fracture toughness decreased dramatically with oxidation temperature in pellets made from microbeads oxidized at temperatures higher than 200°C.

![Graph showing fracture toughness and bulk density of pellets](image)

Figure 4.10: Fracture toughness and bulk density of pellets graphitized at 2400°C for 2 hours as a function of oxidation temperature. The microbeads were oxidized 8 hours at the designated temperature in air.

It is generally believed that the self-sinterability of mesophase materials comes from the beta-resin, the toluene insoluble and pyridine soluble fraction. The result discussed above indicate that at temperatures between 420-500°C, this beta-resin softens [27] [21] and binds the microbeads together through polymerization reactions. Because of the low molecular weight, simple structure and relatively high content of functional groups, beta-resin will be the first fraction to be oxidized during oxidation pretreatment. The oxidized materials have higher melting points and as a result, the oxidized beta resin never softens during heat treatment. This significantly decreases the functionality of beta-resin as a binder. As a result, the mechanical properties of the graphitized pellets

55
decrease. When the oxidation temperature is too high, above 200°C for these particular microbeads, oxygen may attack the mesophase to form a quinone-like structure, which decomposes to give carbon monoxide during high temperature treatment as shown in the mass spectroscopy analysis. This significantly increases the porosity of the final product and consequently the mechanical properties decrease dramatically.

4.2. Conclusion

The carbonization process of both original and oxidized microbeads was studied by characterizing the weight change, structure variation, off-gas composition and shrinkage behavior during carbonization. Results showed that if beta resin is oxidized, its functionality as an in-situ binder is impaired. As a result, the liquid phase sintering mechanism that is important to create the ‘bridges’ between microbeads may be lacking in the carbonization of oxidized microbeads. In situ analysis of off-gas composition by thermogravimetric-mass spectroscopy shows that the chemical processes leading to dehyrogenation are responsible for sample shrinkage. The observation that fracture toughness of graphitized pellets decreases with an increase in oxidation temperature suggests that oxidation pretreatment should be avoided when maximum fracture properties are desired.
CHAPTER 5:
EFFECT OF HEAT TREATMENT TEMPERATURE ON PROPERTIES OF
TiB$_2$ REINFORCED CARBON COMPOSITE

In the search for a good reinforcement we found an interesting phenomenon: liquid formed in a TiB$_2$/C composite when heat treated at or above 2800K. Even more interesting is that the fracture toughness of the graphitized pellet become higher at relative low loadings. In this chapter, a systematic investigation is described that was conducted to evaluate the impact of eutectic liquid formation on the performance of TiB$_2$/C composite.

While the low temperature liquid phase sintering (500-800K) was discussed by many authors, rather limited information is available regarding eutectic liquid formation in carbon composites and how it affects the material properties. Garcia-Rosales et al. noticed that the catalytic ability on graphitization as measured by the lowest graphitization temperature (initiation temperature of $L_c$ growth) of various carbides follows the same trend as the corresponding eutectic liquid formation temperature [45]. Mechanical properties of the composites heat treated at the extreme temperature (2900°C) when eutectic liquid forms were unfortunately not reported. On the other hand, eutectic liquid formation was found to be detrimental to the mechanical properties of the “matrix inhibited C/C composite”[67, 68]. The authors ascribe it to fiber damage/crystallization. Recently two groups reported increased mechanical properties due to addition of
reinforcements. Tong et al. observed dramatic increase in flexural strength when boron was added to the Zr-doped carbon[62]. The composite was hot pressed to 2600°C, higher than the eutectic liquid formation temperature. Wen et al. synthesized W_{2}B_{5}/C composite with excellent mechanical properties via \textit{in situ} reaction sintering by hot pressing at 2000°C. Although the sintering temperature is less than the eutectic liquid formation temperature, the authors suspect that the real temperature could be much higher due to exothermic chemical reaction. In all cases, the formation of liquid in carbon composite seems to be accompanied with rather dramatic change in material properties.

![TiB_2-C phase diagram](image)

**Figure 5.1:** TiB_{2}-C phase diagram

As shown in Fig 5.1, eutectic liquid which contains 32mol% carbon, forms at 2507°C in the TiB_{2}-graphite system. According to R.M. German, typically liquid phase sintering temperature would be slightly above the eutectic temperature[86].
TiB₂ of two different grades was used in the experiments, with particle sizes less than 325mesh (Alfa materials, 99.5%, metal basis) and less than 10 microns (Sigma-Aldrich) respectively. The TiB₂/C composites were heat treated at four different temperatures: 2300K, 2700K, 2800K and 2900K. The variation of materials properties, such as density, extent of graphitization, pore size distribution, microstructure, fracture performance, etc, were investigated with a focus on property changes around the eutectic temperature. The other advantage of using borides as reinforcement is that they also act as oxidation inhibitor due to the formation boron oxide. Because of this, the oxidation behavior of the composite was also investigated.

5.1. Results and Discussions

5.1.1. Properties of the Sintered Pellets

Table 5.1 list the properties of pellets heat treated at 2300, 2700, 2800 and 2900K for 2hrs. They are the average of 5 experiments. Slight variation in density, weight loss and shrinkage of the pellets made from pure microbeads were observed by increasing the graphitization temperature from 2300K to 2700K, but they remain almost constant at higher heat treatment temperatures. With the addition of TiB₂ (325 mesh), the density of the green and heat treated pellets increased, but shrinkage decreased with the increase in TiB₂ content. At 20vol% TiB₂ doping, the volume shrinkage decreased from 42% to around 32%. This result indicates that the addition of hard TiB₂ particles inhibits the shrinkage of the composite materials during heat treatment, and potentially leads to higher porosity level in the sintered product. Interestingly, all pellets with TiB₂ additions
TABLE 5.1
PROPERTIES OF GRAPHITIZED CARBON PELLETS WITH AND WITHOUT TiB$_2$ (325 MESH) ADDITIONS

<table>
<thead>
<tr>
<th>Materials</th>
<th>Green Density (g/cm$^3$)</th>
<th>Final Density (g/cm$^3$)</th>
<th>Linear Shrinkage (%)</th>
<th>Volume Shrinkage (%)</th>
<th>Weight Loss (%)</th>
<th>Fracture Toughness (Mpa.m$^{0.5}$)</th>
<th>$D_{002}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mcmb, pure, 2300K</td>
<td>1.27</td>
<td>1.92</td>
<td>16.2</td>
<td>41.4</td>
<td>11.5</td>
<td>1.53</td>
<td>0.3422</td>
</tr>
<tr>
<td>Mcmb, pure, 2700K</td>
<td>1.27</td>
<td>1.95</td>
<td>16.8</td>
<td>42.4</td>
<td>11.7</td>
<td>1.39</td>
<td>0.3380</td>
</tr>
<tr>
<td>Mcmb, pure, 2800K</td>
<td>1.27</td>
<td>1.96</td>
<td>16.6</td>
<td>42.3</td>
<td>11.4</td>
<td>1.28</td>
<td>0.3379</td>
</tr>
<tr>
<td>Mcmb, pure, 2900K</td>
<td>1.28</td>
<td>1.95</td>
<td>16.9</td>
<td>42.4</td>
<td>11.7</td>
<td>1.36</td>
<td>0.3376</td>
</tr>
<tr>
<td>Mcmb, 5vol%TiB$_2$, 2300K</td>
<td>1.37</td>
<td>2.02</td>
<td>15.7</td>
<td>39.8</td>
<td>10.9</td>
<td>1.38</td>
<td>0.3392</td>
</tr>
<tr>
<td>Mcmb, 5vol%TiB$_2$, 2700K</td>
<td>1.36</td>
<td>2.03</td>
<td>16.0</td>
<td>40.5</td>
<td>10.8</td>
<td>1.30</td>
<td>0.3370</td>
</tr>
<tr>
<td>Mcmb, 5vol%TiB$_2$, 2800K</td>
<td>1.35</td>
<td>1.98</td>
<td>15.2</td>
<td>39.1</td>
<td>10.9</td>
<td>1.61</td>
<td>0.3359</td>
</tr>
<tr>
<td>Mcmb, 5vol%TiB$_2$, 2900K</td>
<td>1.36</td>
<td>1.96</td>
<td>14.9</td>
<td>38.3</td>
<td>11.0</td>
<td>1.62</td>
<td>0.3358</td>
</tr>
<tr>
<td>Mcmb, 10vol%TiB$_2$, 2300K</td>
<td>1.45</td>
<td>2.09</td>
<td>14.5</td>
<td>37.6</td>
<td>9.9</td>
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<tr>
<td>Mcmb, 10vol%TiB$_2$, 2700K</td>
<td>1.44</td>
<td>2.10</td>
<td>15.0</td>
<td>38.2</td>
<td>9.9</td>
<td>1.31</td>
<td>0.3368</td>
</tr>
<tr>
<td>Mcmb, 10vol%TiB$_2$, 2800K</td>
<td>1.45</td>
<td>2.10</td>
<td>14.6</td>
<td>37.7</td>
<td>9.8</td>
<td>1.30</td>
<td>0.3369</td>
</tr>
<tr>
<td>Mcmb, 10vol%TiB$_2$, 2900K</td>
<td>1.45</td>
<td>2.03</td>
<td>13.8</td>
<td>35.7</td>
<td>9.9</td>
<td>0.63</td>
<td>0.3352</td>
</tr>
<tr>
<td>Mcmb, 20vol%TiB$_2$, 2300K</td>
<td>1.62</td>
<td>2.19</td>
<td>12.3</td>
<td>32.3</td>
<td>8.4</td>
<td>1.19</td>
<td>0.3384</td>
</tr>
<tr>
<td>Mcmb, 20vol%TiB$_2$, 2700K</td>
<td>1.62</td>
<td>2.21</td>
<td>13.3</td>
<td>33.3</td>
<td>8.7</td>
<td>1.31</td>
<td>0.3364</td>
</tr>
<tr>
<td>Mcmb, 20vol%TiB$_2$, 2800K</td>
<td>1.62</td>
<td>2.17</td>
<td>12.4</td>
<td>31.9</td>
<td>8.7</td>
<td>1.18</td>
<td>0.3350</td>
</tr>
<tr>
<td>Mcmb, 20vol%TiB$_2$, 2900K</td>
<td>1.62</td>
<td>2.14</td>
<td>12.5</td>
<td>31.6</td>
<td>9.4</td>
<td>1.01</td>
<td>0.3350</td>
</tr>
</tbody>
</table>

show the same trend that density and shrinkage increase initially with the increase in heat treatment temperature, but then start to decrease when they were heat treated at 2800K or higher. This is thought to be caused by the eutectic liquid formation, as will be discussed later. TiB$_2$ also shows the ability to catalyze the microbeads graphitization process. The $d_{002}$ spacing of pellets with TiB$_2$ doping is less than that of pellets made from pure microbeads. The catalytic effect increases with the increase in TiB$_2$ content. Pellets with 10vol% TiB$_2$ addition heat treated at 2900K and pellets with 20vol% TiB$_2$ addition heat treated at 2800 and 2900K have a $d_{002}$ spacing even less than that of pure graphite, which is 3.354Å.
The catalytic effect of TiB$_2$ additions on graphitization of microbeads was further analyzed by heat treating 20vol% TiB$_2$/MCMB composites at various temperatures for 2hrs. The X-ray diffraction patterns of the graphitized pellets are shown in Fig 5.2. The position of the C$_{002}$ peak shifts gradually to a higher value with an increase in heat treatment temperature. The appearance of the C$_{102}$ peak, when the pellets were heat treated at 2800K or higher, indicates the formation of a 3-D graphitic structure. Besides C and TiB$_2$ phases, TiC was also detected. The peak intensity remained almost constant until 2700K, after which it increased with graphitization temperature. No boron or boron carbide phase was detected in all cases. Additional experiments were conducted to determine the mechanism of TiC formation at low temperatures and we conclude that it is the result of impurities that existed in the raw materials. First of all, boron oxide and
titanium oxide were found in the surface layer of TiB₂ particles by XPS analysis (Kratos XSAM 800 Spectrometer), and a small amount of oxygen incorporation into the microbeads is inevitable since the experiments were conducted in air. Secondly, trace amounts of Ti₂O₃ and TiBO₃ phases were detected in the XRD pattern of pellets heat treated at 1000°C. Thirdly, incorporation of more oxygen into microbeads by pre-oxidation was found to increase the intensity of TiC phase in the heat treated product, while addition of 1wt% of B inhibits any formation of TiC. These results indicate that formation of TiC is determined by the ratio of Ti, B, and O elements in the raw mixture. Boron oxide has a very low melting point of 450°C and it is highly mobile at higher temperatures. It may diffuse into and react with the carbon matrix, with the titanium forming TiC.

Figure 5.3: Variation of d₀₀₂ spacing of carbon pellets made from pure and 1wt% boron, 20vol% TiB₂ (325 mesh) doped microbeads as a function of heat treatment temperature.
The variation of $d_{002}$ spacing of pure, 1wt%B and 20vol%TiB$_2$ doped microbeads as a function of heat treatment temperature is shown in Fig 5.3. The extent of graphitization of pure microbeads increases gradually with an increase in the heat treatment temperature. Boron and TiB$_2$ exhibit a catalytic effect on graphitization starting from around 2100K. A similar result was reported by Becker et al. when they studied the sintering behavior of boron-substituted polyaromatic mesophase[59]. Their catalytic ability as a function of temperature is strikingly similar at temperatures lower than 2700K, which may be a reflection of the similarity of the mechanism of their catalytic behavior. At higher temperatures, the $d_{002}$ spacing of the boron doped pellets remains almost constant while for TiB$_2$ doped pellets it quickly decreases to a value less than that of pure graphite, indicating the formation of a highly ordered graphitic structure and the diffusion of boron into the carbon matrix. The increase in TiC formation is the result of this boron loss.

The fracture toughness of pellets made from pure microbeads decreases in general with an increase in heat treatment temperature. The effect of heat treatment temperature on the fracture toughness of composites with TiB$_2$ additions is much more complicated. For pellets with 5vol% TiB$_2$ additions, the fracture toughness decreases initially with an increase in heat treatment temperature up to 2700K, similar to that of pellets made from pure microbeads. However an additional gain of 24% was achieved by increasing the graphitization temperature further. The fracture toughness value of 10vol% TiB$_2$/MCMB remains almost constant at 1.3MPa.m$^{0.5}$ at temperatures lower than 2900K, then it decreases drastically to 0.63MPa.m$^{0.5}$. For pellets with 20vol% TiB$_2$ addition, a slight gain was observed by increasing graphitization temperature to 2700K but then it declined.
with further increase in heat treatment temperature. If one considers this phenomenon from a different perspective, i.e., by analyzing the effect of TiB₂ content at a given temperature, one finds that at the relatively low heat treatment temperature of 2300K, addition of TiB₂ particles leads to a decrease in fracture toughness, possibly due to an increase in porosity of the sintered products. Different trends were observed when composites were heat treated at higher temperatures. For example, with a heat treatment temperature of 2700K, the fracture toughness of composites with 5, 10, 20vol% of TiB₂ addition were almost identical, and lower than that of pellets without an additive, while for composites heat treated at 2900K, pellets with 5vol% TiB₂ addition give the highest fracture toughness. The resistance to fracture propagation decreased drastically to 0.63MPa.m⁰.⁵ by increasing the dopant content to 10vol%, but by further increasing the TiB₂ content the fracture toughness increases again. Microstructure analysis was performed to better understand the observed variation in mechanical properties.

5.1.2. Microstructure Analysis

5.1.2.1 Fractography

The fractured surfaces after mechanical testing were observed in an SEM under both secondary electron and backscattering modes. The titanium containing phase, due to the higher atomic number of titanium, has higher brightness in the backscattered image. Hence, the backscattered images provide information on the distribution of TiB₂/TiC in the fractured surface layer and they were taken at the same spot as the corresponding secondary electron images. Detailed studies were conducted on composites with 5 and 20
volume percent of TiB₂ addition, and the evolution of microstructure as a function of heat treatment temperature is shown in Fig 5.4 and Fig 5.5 respectively.

The fractured surfaces of pellets with TiB₂ additions heat treated at 2300K show similar morphology to that of pellets made from pure microbeads. Both the bimodal size distribution of the mesophase particles and their original shapes are well maintained after heat treatment. TiB₂ particles are dispersed randomly in the surface layer, and there is no sign of strong interaction between TiB₂ and the surrounding matrix. After treatment at 2700K, smaller TiB₂ particles were found around the original TiB₂ particles, indicating the diffusion of TiB₂ to the surrounding matrix. For the most part, the microbeads still have their original morphology, but around the smaller TiB₂ particles a flake-like structure was observed, as shown in Fig 5.4(c). A dramatic change in morphology was seen when pellets were heat treated at 2800K and 2900K. In Fig 5.4(e) and Fig 5.4(g), mesocarbon microbeads have transformed into small flake-like structures, and the original round shape has disappeared. The TiB₂ particles are distributed rather uniformly in the carbon matrix and their size has become much smaller. For composites with 20vol% TiB₂ addition, heat treatment at such high temperature leads to the formation of large graphite crystals, as shown in Fig 5.5(e) and Fig 5.5(g), with TiB₂ located at the boundary of adjacent crystals. Complex structures were always seen wherever TiB₂ particles were present. This may indicate that TiB₂ acts as a deflection point for crack propagation, which explains why composites with 20vol% TiB₂ addition have higher fracture toughness than pellets with 10vol% TiB₂ addition when they were heat treated at
Figure 5.4: Secondary electron micrographs of fresh fractured surfaces of 5vol%TiB₂ (325 mesh)/MCMB heat treated at (a)2300K, (c)2700K, (e)2800K, (g)2900K for 2hrs. Corresponding backscattered electron images (b), (d), (f), (h) of the same regions.
Figure 5.5: Secondary electron micrographs of fresh fractured surfaces of 20vol% TiB₂(325 mesh)/MCMB heat treated at (a) 2300K, (c) 2700K, (e) 2800K, (g) 2900K for 2hrs. Corresponding backscattered electron images (b), (d), (f), (h) of the same regions.
2900K. The TiB$_2$ particle is no longer seen as a continuous particle, but rather as part of a layered structure consisting of graphite flakes located between Ti-containing layers.

In Fig 5.6, a graphite crystal is seen that fractured during mechanical testing, revealing many layers. The fracture of graphite in this mode requires very little energy, so the fracture toughness decreases whenever large graphite crystals form during heat treatment. A “transition layer” was found between the graphite crystals and the Ti-containing phase, which may be the origin of the graphite crystal growth.

5.1.2.2 Optical Microstructure

The optical images of the polished surfaces of composites with 5 and 20vol% TiB$_2$ addition are shown in Fig 5.7. After heat treatment at 2300K, both microbeads and TiB$_2$ particles still have their original shape. Evidence of TiB$_2$ diffusion into the carbon matrix was found in samples processed at 2700K. For pellets with 5vol% TiB$_2$ addition,
Figure 5.7: Optical micrographs of carbon composites with 5vol% (a-d) and 20vol% (e-h) TiB$_2$ (325 mesh) additions and heat treated at (a, c) 2300K, (b, f) 2700K, (c, g) 2800K, (d, h) 2900K for 2hrs.
graphitization at higher temperature leads to a homogenous distribution of TiB$_2$ particles and their size becomes much smaller. For pellets with 20vol% TiB$_2$ addition, graphitization leads to the formation of a layered structure, which shows direct evidence of eutectic liquid formation. The overall size of the layered structure is much larger than the original size of the TiB$_2$ particles, indicating the aggregation/growth of the TiB$_2$ particles with the help of the eutectic liquid. In DIC mode, detailed analysis revealed that the bright areas are actually composed of two phases. EDAX analysis indicates that the relatively dark areas are TiC, as indicated by arrows in Fig 5.7(g) and Fig 5.7(h), while the relatively bright regions are TiB$_2$. The observations on the polished sections correlate very well with the fractography results.

5.1.3. Particle Size Effect

The microstructure analysis indicates that the diffusion of TiB$_2$ particles into the surrounding matrix resulting in the formation of smaller particles plays a big role in the observed enhancement in fracture properties. In this section, results are presented from using a different grade of TiB$_2$, with particle size less than 10 micron as a dopant. The pellets were heat treated at 2800K and their properties are listed in Table 5.2. The density of green and graphitized pellets is very similar to that of pellets with 325 mesh TiB$_2$ additions at the same TiB$_2$ content, with a difference less than 1%. The shrinkage of pellets with finer TiB$_2$ additions is slightly higher. The d$_{002}$ spacing of carbon and weight loss during heat treatment are also very similar. Their fracture toughness, however, is significantly higher. The best performance was obtained with 10vol% of TiB$_2$ addition, which has a fracture toughness value of 1.92MPa.m$^{0.5}$, a 50% increase compared with
that of pellets made from pure microbeads. The microstructure of the composite with 10vol% TiB$_2$ addition is similar to what we observed on composite with 5vol% TiB$_2$ (325mesh) addition. The microbeads were transformed into small flakes and the TiB$_2$ particles were distributed uniformly in the carbon matrix with a much smaller size.

### TABLE 5.2

**PROPERTIES OF GREEN AND GRAPHITIZED CARBON PELLETS WITH TiB$_2$ (<10 MICRON) ADDITIONS**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Green Density (g/cm$^3$)</th>
<th>Final Density (g/cm$^3$)</th>
<th>Linear Shrinkage (%)</th>
<th>Volume Shrinkage (%)</th>
<th>Weight Loss (%)</th>
<th>Fracture Toughness (Mpa.m$^{0.5}$)</th>
<th>D$_{50}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mcmb, 2.5vol%TiB$_2$, 2800K</td>
<td>1.32</td>
<td>1.98</td>
<td>15.8</td>
<td>41.3</td>
<td>11.9</td>
<td>1.49</td>
<td>0.383</td>
</tr>
<tr>
<td>Mcmb, 5vol%TiB$_2$, 2800K</td>
<td>1.35</td>
<td>1.98</td>
<td>15.3</td>
<td>39.8</td>
<td>11.8</td>
<td>1.72</td>
<td>0.3362</td>
</tr>
<tr>
<td>Mcmb, 7.5vol%TiB$_2$, 2800K</td>
<td>1.39</td>
<td>2.07</td>
<td>15.3</td>
<td>40.1</td>
<td>10.9</td>
<td>1.72</td>
<td>0.3361</td>
</tr>
<tr>
<td>Mcmb, 10vol%TiB$_2$, 2800K</td>
<td>1.43</td>
<td>2.09</td>
<td>14.5</td>
<td>38.7</td>
<td>10.5</td>
<td>1.92</td>
<td>0.3364</td>
</tr>
<tr>
<td>Mcmb, 20vol%TiB$_2$, 2800K</td>
<td>1.59</td>
<td>2.19</td>
<td>13.2</td>
<td>34.7</td>
<td>9.8</td>
<td>1.44</td>
<td>0.3348</td>
</tr>
</tbody>
</table>

The typical load-displacement curves recorded during mechanical testing are shown in Fig 5.8. Pellets made from pure microbeads fracture in a brittle fashion. The crack propagates rapidly after initiation, and gives a smooth fractured surface. Higher loads are required to fracture the pellets with 5 and 10vol% TiB$_2$ additions, which indicates that the resistance of those materials to crack propagation is higher. The fracture process, although not as brittle as that of pellets made from pure microbeads, still gives a quite smooth fractured surface, while a much rougher surface was obtained during mechanical
Figure 5.8: Typical load-displacement diagrams recorded during fracture testing of carbon pellets graphitized at 2800K for 2hrs, with (a) 0%, (b) 5vol%, (c) 10vol%, (d) 20vol% TiB₂(<10micron) additions.

testing for pellets with 20vol% TiB₂ additions. The process of crack propagation is much more stable although the maximum load decreases.

The pore size distribution of microbeads pellets heat treated at 2800K, 10vol% TiB₂(10 μm)/C heat treated at 2300K, 2800K and 20vol% TiB₂/C heat treated at 2800K are shown in Fig 5.9. The y-axis, differential intrusion, is the derivative of mercury intrusion by pore size. The total pore volumes as measured by the mercury porosimeter are 10.6%, 16.3%, 16.5% and 19.9% respectively. Clearly, addition of additives increased the total porosity level. Strong correlation was found between fracture toughness and average pore sizes, i.e., composites with smaller average pore size tended to have high toughness. The average pore size of the pellets with 10vol% TiB₂ addition is one order of magnitude smaller than that of pellets made of microbeads alone and heat
treated at the same temperature, 2800K. At higher TiB$_2$ loading, fracture toughness decreased and the average pore size increased. On the other hand, heat treatment below the eutectic temperature didn’t have much impact on the pore size distribution; instead the average pore size increased a bit, possibly because of the resistance to shrinkage due to the existence of foreign materials.

Figure 5.9: Pore size distribution: (A) microbeads pellet, 2800K, 10vol%TiB$_2$(10µm)/C heat treated at (B) 2300K, (C) 2800K and (D) 20vol%TiB$_2$/C, 2800K.

5.1.4. Quantification of Boron Concentration in the Carbon Matrix

It is well known that boron, when heat-treated at temperatures higher than 1500°C with carbon, will diffuse into the graphite lattice and substitute for carbon in the graphite structure, as evidenced by the lowered d$_{002}$ space[87]. Boron addition to carbon materials accelerates the graphitization process [88], increases their resistance to oxidation [61], and can alter their mechanical properties [58]. It is important to note that previous studies
Figure 5.10: Qualitative LA-ICP-MS raster scan performed on a freshly fractured graphite crystal surface. The 20vol%TiB$_2$ (325 mesh)/MCMB composite was graphitized at 2900K for 2hrs. Note the relatively flat fractured surface in focus in the image. An 8 micron laser beam is used in the experiment.
have proved that the impact of boron is most obvious when significant amounts of boron are present. These results suggest a need for a reliable and fast method for the determination of boron concentrations in carbon materials. We report a first attempt to quantify boron concentrations in a carbon matrix using laser ablation ICP-MS (LA-ICP-MS).

Direct evidence of boron diffusion into the carbon matrix was obtained by performing a qualitative B and Ti analysis by LA-ICP-MS. We performed this qualitative raster analysis on a graphite crystal located on the fractured surface of a carbon pellet with 20vol% TiB$_2$ (325mesh) addition that was heat treated at 2900K. This allowed us to raster the laser beam on only one graphite crystal and minimized the interference from neighboring TiB$_2$ particles. As seen in Fig 5.10(c), when ablation was initiated at t=25s, the signal of boron detected by mass spectrometry increased by 6-7 times, while the titanium signal remained constant.

Quantitative analysis was performed on the polished surfaces. Microbeads with 1wt% boron addition and heat treated at 2700K for 2hrs were used as calibration standard. Research of Cermignani et al. showed that boron diffusion into a carbon matrix is already very fast at 2300°C [88]. Here we chose a slightly higher heat treatment temperature at 2700K where graphite has higher boron solubility. The calibration standard was prepared and heat-treated in the same way as the TiB$_2$ doped pellets. We assume that the difference in ablation volume between samples and the calibration standard are negligible due to their matching matrices. The analysis of 20vol% TiB$_2$(325 mesh)/MCMB composite heat-treated at 2800K and 2900K was conducted in raster scan mode using a 30 micron laser beam, which served to increase sensitivity and improve signal stability.
representative time-resolved intensity plot of $^{11}\text{B}$ and $^{47}\text{Ti}$ signals during laser rastering across the calibration standard is shown in Fig 5.11. Constant carbon and boron signals were observed during a 30 micron raster scan, which confirmed the compositional homogeneity of the calibration standard. We measured a boron concentration of 1.06 wt% in the 2900K sample and 0.97 wt% in the 2800K sample. We employed 15 micron spot analyses to quantify boron in the pellets heat treated at 2300K. We measured an average boron concentration of 0.49 wt% in the 2300K pellets. A small amount of Ti was also detected in the calibration standard and all measured samples. The observed Ti counts were nearly two orders of magnitude lower than the boron counts, and thus are most likely due to an impurity contained in microbeads.
In the first section above, we studied the catalytic behavior of 1wt%B and 20vol% TiB$_2$ doped microbeads. Since no boron or boron carbide phase was identified in the XRD analysis, it is clear that the boron that diffused into the carbon matrix does not cause the formation of large graphite crystals. Moreover, the 1wt%B/MCMB heat treated at 2800K for 2hrs fractured in a brittle mode and has a fracture toughness of 1.04MPa.m$^{0.5}$, which is lower than that of pellets made from pure microbeads. Hence, the formation of the eutectic liquid is responsible for the observed variation in microstructure and mechanical behavior.

Figure 5.12: Weight loss as a function of oxidation time of pellets made from (a) pure microbeads, and microbeads with (b) 5vol%, (c) 10vol%, (d) 20vol% TiB$_2$($<10\mu$m) additions and microbeads with (e) 5vol%, (f) 10vol%, (g) 20vol% TiB$_2$ (325 mesh) additions.
5.1.5. *Oxidation Resistance*

The oxidation rate of the composites heat treated at 2800K is shown in Fig 5.12. The experiments were carried out in dry air flow and the temperature was maintained at 800°C. The pellets made from original microbeads oxidize readily at this temperature, while the pellets with TiB₂ additions have a significantly lower rate of weight loss. For pellets with finer TiB₂ (<10 micron) additions, the inhibition effect increases with the amount of TiB₂ added to the composite. The ratio of weight loss rate of pellets made from microbeads with 0%, 5%, 10%, 20vol% of TiB₂ addition was 223:4.7:3.7:1, at 4% burn off. The resistance to oxidation of pellets with coarser TiB₂ addition (325 mesh) was much worse when same volume percent of TiB₂ was added. The resistance of pellets with 5vol% TiB₂ addition is better than pellets with 10vol% addition. As we have already noted, porosity increases with an increase in TiB₂ content. The increase of pore volume means more paths for oxygen diffusion and an increased weight loss. The experimental result is the consequence of the competition between the above two factors.

One of the pellets, with 20vol% of TiB₂ (325 mesh) addition, was crushed into fine powders and subjected to thermal analysis, and the result, together with that of pure TiB₂ powder, are shown in Fig 5.13. A weight increase was observed at temperatures as low as 500°C for both samples, and their DTA profiles are similar at temperatures less than 800°C (e.g., both have an exotherm at ~520°C). Clearly TiB₂ particles were oxidized before carbon starts to be burned off. X-ray diffraction confirmed that the surface of the oxidized TiB₂/C composite was covered by a layer of TiO₂ (rutile). The formation of boron oxide as the result of the oxidation reaction of TiB₂ protects the carbon matrix from being oxidized.
5.2. Conclusions

TiB$_2$/C composite materials with enhanced mechanical properties and oxidation resistance were prepared from doped mesocarbon microbeads. Eutectic liquid forms between TiB$_2$ and carbon at temperatures below 2800K and the resultant layered structure was observed in microstructure analysis. The diffusion of TiB$_2$ into the surrounding matrix happens at even lower temperatures. Low level doping of TiB$_2$ leads to formation of small liquid domains and an imperfect graphite structure, which is beneficial to mechanical properties. Higher levels of TiB$_2$ additions lead to formation of large liquid domains and perfect graphite crystal structures, which degrades mechanical properties since graphite is fragile. Better fracture properties were obtained when smaller TiB$_2$ particles were used. Average size of pores becomes much smaller due to liquid formation.
and in general, a composite with smaller pores tends to have better toughness. The TiB$_2$ additions increase the resistance of carbon to oxidation. TGA-DTA experiments proved that TiB$_2$ was oxidized before carbon was burned off and that the oxidation product, boron oxide, should be the real source of the oxidation inhibition effect.

Laser ablation ICP-MS and XRD results indicate that boron enters into the carbon matrix around the eutectic liquid formation temperature. Since the amount of boron entering into the carbon matrix is rather small, about 1wt%, its impact on the extent of graphitization and fracture property is limited. These results indicate that the enhanced mobility of TiB$_2$ with the help of liquid formation is the cause of the observed increase in the extent of graphitization and improved mechanical properties.
CHAPTER 6:
EXTENDED INVESTIGATION ON THE EFFECT OF ADDITIVES ON PROPERTIES
OF MESOCARBON MICROBEAD-BASED CARBON COMPOSITES

In the previous chapter we demonstrated how eutectic liquid formation improved the mechanical performance of carbon composites based on mesocarbon microbeads. In this chapter, the same approach was extended to several other liquid formation capable systems: TiC/C, ZrB₂/C and Ni/C. The exploration for better reinforcements led to testing of other potential additives, such as short carbon fiber, aluminum metal and titanium nitride, etc, and results for these systems are also presented in this chapter.

6.1. Liquid Formation Capable Composites

6.1.1. TiC/C

Eutectic liquid that contains 26.2 at.% carbon forms at 2776°C in TiC-graphite [56]. In order to generate eutectic liquid, some pellets were heat treated at 2800°C at Oak Ridge National Lab (ORNL). The rest of the heat treatments were conducted at Notre Dame.

Properties of the green and heat treated pellets are shown in Table 6.1. TiC was introduced by either addition of TiC powder or through in situ reaction of Ti with carbon.


<table>
<thead>
<tr>
<th>Materials</th>
<th>Green Density (g/cm³)</th>
<th>Final Density (g/cm³)</th>
<th>Linear Shrinkage (%)</th>
<th>Volume Shrinkage (%)</th>
<th>Weight Loss (%)</th>
<th>Fracture Toughness (Mpa.m⁰.⁵)</th>
<th>D₀₀₂ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mcmb, pure, 2700K</td>
<td>1.27</td>
<td>1.95</td>
<td>16.8</td>
<td>42.4</td>
<td>11.7</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>1.24</td>
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<tr>
<td>Mcmb, 5vol%Ti, 2700K</td>
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<td>41.4</td>
<td>11.0</td>
<td>1.22</td>
<td>3.3770</td>
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<td>40.7</td>
<td>10.1</td>
<td>1.26</td>
<td>3.3767</td>
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<tr>
<td>Mcmb, 20vol%Ti, 2700K</td>
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<td>2.31</td>
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<td>38.5</td>
<td>8.8</td>
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<td>3.3715</td>
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<td>Mcmb, 5vol%Ti, 3073K</td>
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<td>Mcmb, 20vol%Ti, 3073K</td>
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<tr>
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<td>10.6</td>
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<td>3.3763</td>
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<tr>
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<td>12.6</td>
<td>31.3</td>
<td>9.1</td>
<td>0.67</td>
<td>3.3684</td>
</tr>
</tbody>
</table>

*Shrinkage in Diameter

At a low heat treatment temperature of 2700K, shrinkage of the pellets decreased with an increase in TiC loading. With 20vol% TiC addition, the volume shrinkage was only 31.3%, while the predicted volume shrinkage is as high as 37.1% if we assume only microbeads shrink during heat treatment and total porosity doesn’t change much. This indicates that shrinkage of the microbeads was hindered by the addition of foreign particles, and should lead to increased porosity levels in the final product. The fracture properties deteriorate continuously with the increase in TiC volume concentration. A 52% decrease in fracture toughness was observed at 20vol% TiC addition.
Titanium metal reacts with carbon to form TiC at temperatures below 1500ºC. Compared with TiC additions, the decrease in shrinkage is much less, and as a result, the density of the heat treated composite is much higher and the porosity level much lower. Two factors contribute to this phenomenon. First of all, fewer foreign particles were added to the mixture at the same final additive level. When TiC is formed \textit{in situ} through a chemical reaction from Ti metal, the carbon element comes from the microbeads. Moreover, although both labeled as -325 mesh, the size of the TiC particles is significantly less than that of Ti, as will be shown later in Fig 6.3. Secondly, the reaction between Ti and C may lead to increased shrinkage. The fracture toughness of the composite is much higher than that of pellets with TiC additions at the same additive level. However, there is almost no improvement compared with pellets made from

![Figure 6.1: Pore size distribution of (a) microbeads pellets, (b) pellets with 20vol% Ti addition. Both pellets were graphitized at 2800ºC](image)
Figure 6.2: Secondary electron micrographs of fresh fractured surfaces of (a) microbeads pellet and pellet with (b) 5vol%Ti, (c) 20vol%Ti addition as well as backscattered electron image of pellet with (d) 20vol% Ti, same regions as (c). All pellets were heat treated at 2800°C.

microbeads alone, although the pellets fractured in a much smoother fashion, similar to what was observed in the TiB\(_2\)/C system.

The pellets with Ti additions were also heat treated at 2800°C. It is worth noting that in all cases, the density of the final product is lower than that of pellets heat treated at 2700K. Fracture toughness values increased continuously with the increase in Ti content. A 20% increase was obtained for pellets with 20vol% Ti addition, compared with pellets made from microbeads alone and heat treated at the same temperature. Pore size
distribution showed the same trend as we observed in the TiB₂/C composites, i.e., pellets with a smaller average pore size have a higher resistance to fracture. As shown in Fig 6.1, the pore size distribution profile of a microbead pellet heat treated at 2800°C is very similar to that of the same pellet heat treated at 2800K (Fig 5.9) but the average pore size became smaller. The average pore size decreased at 20vol% Ti addition. The measured open porosity for the the microbead pellet and the pellet with Ti additions are 10.0% and 22.0% respectively.

TiC acted as a catalyst for the graphitization of mesocarbon microbeads. The extent of graphitization, as indicated by the lower d₀₀₂ spacing, is higher for pellets with

Figure 6.3:  Optical micrographs of carbon composites (a) 10vol% TiC, 2700K, (b) 20vol% Ti, 2700K, (c) 5vol% Ti, 2800°C, (d) 20vol% Ti, 2800°C.
TiC additions at the same additive level when heat treated at the same temperature, possibly because of the larger contact area between TiC and microbeads due to the smaller size of the TiC particles. For pellets with 20vol% Ti addition and heat treated above the eutectic liquid formation temperature at 2800ºC, the \( d_{002} \) spacing, 0.3355, is very close to that of natural graphite, which is 0.3354. Some large graphite crystals were observed on the fracture surface as shown in Fig 6.2(c). The diffusion of TiC to the surrounding carbon matrix was observed at 2700K, and leads to a homogenous distribution of TiC particles in the carbon matrix, at much smaller size, in composites with 5vol% Ti addition and heat-treated at 2800ºC, as demonstrated in Fig 6.3(c). At higher loadings, the particle sizes seen in the polished cross sections become much larger.

6.1.2. ZrB\(_2\)/C

Eutectic liquid forms in the ZrB\(_2\)-graphite at 2390ºC and it contains 33 at.% carbon[56]. The pellets were heat treated at 2300K and 2700K for 2hrs. Properties of the green and heat treated pellets are shown in Table 6.2.

Similar to TiC/C composites, heat treatment at temperatures lower than the eutectic liquid formation temperature didn’t provide any help in improving the fracture properties. On the other hand, a 30% increase in fracture toughness was achieved by adding 10vol% ZrB\(_2\) powder and heat-treating above the eutectic temperature at 2700K. Shrinkage of the pellets decreased at higher heat treatment temperature similar to what was observed in the TiB\(_2\)/C composite. Ti and Zr are elements of the same group and their chemical properties are very similar. ZrB\(_2\) forms a eutectic liquid with carbon at a very similar carbon concentration but at a slightly lower temperature. The development in
microstructure is also very similar to what was observed in the TiB₂/C composites. For example, diffusion of the ZrB₂ to the surrounding carbon matrix was observed in pellets heat treated at 2300K and for pellets with 5vol% ZrB₂, while heat treatment at 2700K leads to a rather homogeneous distribution of small ZrB₂ particles in the carbon matrix. ZrB₂ acted as a catalyst for the graphitization process too. The d₀₀₂ spacing of pellets with 20vol% ZrB₂ addition and heat treated at 2700K is less than that of natural graphite, and large graphite crystals were observed on the fractured surface. A small amount of ZrC was identified in the XRD profile. The pellets with the best fracture toughness were subject to mercury intrusion testing and the pore size distribution was found to be very

<table>
<thead>
<tr>
<th>Materials</th>
<th>Green Density (g/cm³)</th>
<th>Final Density (g/cm³)</th>
<th>Linear Shrinkage (%)</th>
<th>Volume Shrinkage (%)</th>
<th>Weight Loss (%)</th>
<th>Fracture Toughness (Mpa·m⁰.⁵)</th>
<th>D₀₀₂ (nm)</th>
</tr>
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<tr>
<td>Mcmb, pure, 2300K</td>
<td>1.27</td>
<td>1.92</td>
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<td>41.4</td>
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<td>1.53</td>
<td>0.3422</td>
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<tr>
<td>Mcmb, pure, 2700K</td>
<td>1.27</td>
<td>1.95</td>
<td>16.8</td>
<td>42.4</td>
<td>11.7</td>
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<td>0.3380</td>
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<td>Mcmb, 5vol%ZrB₂, 2300K</td>
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<td>Mcmb, 5vol%ZrB₂, 2700K</td>
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<td>10.8</td>
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<tr>
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<td>2.14</td>
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<td>Mcmb, 10vol%ZrB₂, 2700K</td>
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<td>2.19</td>
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<td>Mcmb, 20vol%ZrB₂, 2700K</td>
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<td>33.6</td>
<td>8.4</td>
<td>1.36</td>
<td>0.3352</td>
</tr>
</tbody>
</table>
similar to that of 10vol% TiB$_2$ (10µm)/C composites heat treated at 2800K, as shown in Fig 6.4, and the open porosity is 17.3%. Again, the average pore size became much smaller due to liquid phase sintering.

6.1.3. Ni/C

Eutectic liquid forms in Ni-graphite at 1326°C and it contains 9.0 at.% carbon [56]. Nickel is a good catalyst for graphitization of carbonaceous materials and its catalytic ability is well documented. In general it is believed that large nickel particles (microns) lead to the formation of graphitic carbon while nanoparticles catalyze the graphitization of turbostratic carbon [73]. Ni/C composites may have very limited practical use as the melting point of nickel is below 1500°C, however, the sintering
behavior and mechanical performance is still very interesting from a theoretical point of view. First of all, nickel doesn't form a stable compound with carbon. Secondly, when large nickel particles are used, their catalytic behavior is different from that of carbides and borides. The TiB$_2$ catalyzed graphitization of mesocarbon microbeads is characterized by the gradual shifting of the C$_{002}$ peak to high angles (Fig 5.2) and complete transformation to graphite at temperatures higher than the eutectic temperature and high TiB$_2$ loadings, while when nickel was used as catalyst, graphitic carbon was observed at heat treatment temperatures as low as 900ºC. As shown in Fig 6.5, the intensity of the 002 diffraction line of the graphitic carbon increased continuously with temperature up to 1700K. The d$_{002}$ spacing of the graphitic carbon is higher than that of

![XRD spectra of carbon composites with 20wt% Ni (5µm) addition and heat treated at different temperatures.](image)

Figure 6.5: XRD spectra of carbon composites with 20wt% Ni (5µm) addition and heat treated at (a) 1173K, (b) 1273K, (c) 1400K, (d) 1500K, (e) 1600K, (f) 1700K and (g) 1900K for 2hrs. Microbeads were pretreated in air at 150ºC.
Figure 6.6: Secondary and backscattered electron micrographs of the nickel particle extended out of the pellet. The sample pellet contains 25wt% of Ni and were heat treated to 1500ºC without dwelling in a dilatometer.

natural graphite. This could be the result of defects in the catalytically formed graphite [81]. If the temperature goes higher, the 002 peak diffraction intensity decreased and we observed large nickel particles on the pellet outer surface, like the one shown in Fig 6.6. The dark area on the outer surface of the large nickel particle seen in the back-scattering image is assumed to be carbon that precipitated out from the melt as it was cooled down. A similar effect was observed when pellets containing 25wt% or more of Ni were heat treated at 1700K.

Similar to what was observed in the TiC/C, TiB₂/C and ZrB₂/C composites, the pellets were found to swell around the eutectic liquid formation temperature. The linear shrinkage of pellets (20wt%/MCMB-150) with different initial densities is shown in Fig 6.7. The swelling event initiates before the eutectic liquid formation temperature. Detailed experiments indicate the swelling event is observable only when the pellets give the highest final densities. The dilatometry experiments were terminated at several
temperatures and XRD results indicate that the swelling event is accompanied by the formation of graphitic carbon phase.

Figure 6.7: Shrinkage behavior of pellets made from oxidized microbeads (air, 8hrs, 150°C) with 20wt% Ni addition and compacted at (a) 175Mpa, (b) 450Mpa, (c) 625Mpa. Experiment conducted in nitrogen gas flow.

The original microbeads were mixed with 5wt% and 20wt% Ni, compacted under 100MPa and heat treated at 1700K for 2hrs. Properties of the pellets before and after heat treatment were compared with those of pellets made from microbeads alone, and are shown in Table 6.3. All pellets made from microbeads alone failed during machining. However, it is clear that pellets with higher Ni loadings have inferior fracture properties. No large graphite crystals were observed on the fracture surfaces as shown in Fig 6.8. The average size of the nickel particles is below 1 µm as shown in the backscattering image.
Pore size distributions as measured by mercury intrusion test of microbead pellets and pellets with 20wt% Ni addition are shown in Fig 6.9. The average pore size of pellets made from microbeads alone, around 0.1µm, is close to that of the same pellets heat treated at much higher temperatures. The nickel particle additions and eutectic liquid formation increased the volume fraction of small pores. However, large pores nucleated during liquid phase sintering which could be responsible for the measured low toughness. The open porosities for the microbead pellet and pellet with 20wt% Ni addition are 8.9% and 17.3% respectively. The increase in porosity is surprisingly large as the volumetric content of Ni in the final product is only roughly 6%. The increase should be the result of volume expansion due to liquid phase sintering.

Nickel acetylacetonate hydrate (NAH), an organic nickel precursor material, was used to introduce nanosized nickel particles. The NAH was first dissolved in acetone, then appropriate amount of microbeads were added to the solution. The solvent was removed by using a rotary evaporator followed by vacuum drying overnight at room temperature.

![SEM Back-scattering](image)

Figure 6.8: Secondary and backscattered electron micrographs of the fractured surface of a 20wt%Ni (5 µm)/MCMB pellet graphitized at 1700K.
Figure 6.9: Pore size distribution of (a) microbead pellet and (b) pellet with 20wt% Ni addition. Both pellets were heat treated at 1700K.

**TABLE 6.3**

**PROPERTIES OF GREEN AND HEAT TREATED PELLETS WITH AND WITHOUT NICKEL ADDITION**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Green Density (g/cm³)</th>
<th>Final Density (g/cm³)</th>
<th>Linear Shrinkage (%)</th>
<th>Volume Shrinkage (%)</th>
<th>Weight Loss (%)</th>
<th>Fracture Toughness (Mpa.m⁰.⁵)</th>
<th>D₉₀₂ (nm)</th>
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<td>Mcmb, 1700K</td>
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<td>0.77</td>
<td>0.3430, 0.3359</td>
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temperature. Chloroform, a much better solvent, was found to effectively remove the
light component, mainly beta resin, from the microbeads and reduce the ability of the
microbeads to self-sinter. X-ray analysis confirmed that only turbostratic carbon was
formed during heat treatment at 1700K. Shrinkage of the pellet is a little higher than that
of microbead pellets (~2%), but the density of the sintered pellet is significantly lower.
The green density of the pellet containing 3wt% Ni addition in the heat-treated product is
1.23g/cm$^3$, when compacted at 100MPa, which is comparable to that of green microbead
pellets. After heat treatment at 1400°C for 2hrs, the density increased to 1.47g/cm$^3$,
significantly less than 1.80g/cm$^3$, density of microbead pellets processed at the same
temperature. The mechanical properties of the pellet apparently are very poor. Two
factors may contribute to the bad performance. First of all, the yield of our organic nickel
precursor material is very low, 23%, and as the molecular structure is dominated by the
organic groups, the initial density should be much less than that of graphite. As a result,
the porosity increase is expected to be significant. Secondly, the organic solvent, acetone,
may extract some of the beta resin and reduce the ability of the microbeads to self-sinter
to some extent, especially since a large amount of solvent was used in the experiment
because of the poor solubility.

6.1.4. Discussion

Liquid phase formation has tremendous impact on the sintering process. First of
all, diffusion rates are much higher in liquid. Secondly, rearrangement of solid particles
by the capillary force effectively reduces porosity [86]. In this work, three representative
additives, TiC, ZrB$_2$ and Ni were investigated for their effect on properties of the heat
treated composites, especially when heat treated around the eutectic liquid formation temperature. Based on the findings and what we obtained in the previous chapter, some of the interesting aspects of liquid phase sintering in carbon composite can be summarized as follows:

1. All pellets swell during the liquid phase sintering. The solubility of the liquid phases in graphite is low and carbon solubility in the liquid phase is high, based on the phase diagrams. Classic sintering theory predicts densification [86]. However, recent studies on the phase transition of graphite showed that the melting of graphite is accompanied by a large increase in volume which can be as much as 70% [89]. The swelling could be the result of local stress caused by the phase transition. In the Ni/C composite, large nickel particles were observed on the outer surface although liquid metals of group VIII elements such as Ni were found to effectively wet the graphite surface [90]. The result supports our reasoning.

2. Fracture properties increase at relative low additive loadings with appropriate heat treatment procedures. It is found that the additive particles diffused into the carbon matrix before the liquid formation temperature. The mechanism of the increase in mechanical properties is not well understood but it may be related to the decreased average pore size due to the presence of the liquid phase. The average pore size turned smaller in all pellets that have higher fracture property than the microbeads pellets processed at the same condition.

3. Formation of the graphite phase leads to decreased fracture properties. All four additives studied acted as good catalysts for the graphitization of...
mesophase carbon. Graphitic carbon formed in the Ni/C composite caused a catastrophic decrease in fracture properties. Large graphite crystals formed in TiB₂/C and ZrB₂/C composites at high additive loadings with heat-treating above the eutectic liquid formation temperature, and the fracture toughness subsequently decreased. Catalytically graphitized materials tend to have inferior mechanical properties, as the isolated graphite crystals do not permit strong bonding [10]. The formation of graphitic carbon is accompanied by the nucleation of large pores that may also contribute to the decreased fracture resistance.

6.2. Other Developments

6.2.1. TiN/C

X-ray diffraction analysis indicates that all TiN transformed to TiC upon heat treatment at 2000°C, in line with thermodynamic calculations. As the chemical reaction of TiN with carbon generates poisonous cyanide gas, and the porosity level is expected to grow significantly because of the high temperature gas release, the investigation didn’t go further.

6.2.2. Milled Carbon Fiber/Carbon Composite

Two milled carbon fibers were used to make C/C composites. The first kind, P-100 fiber, is claimed to be composed of pure carbon but wasn’t graphitized as supported by XRD analysis. The P-100 fiber was also ball-milled in ethanol for 12hrs to reduce the average
length. The fiber and microbeads were mixed homogeneously in isopropanol in an ultrasonicator. Heat was applied during mixing and air was used as a carrier gas for the isopropanol vapor, to aid mixing and to accelerate the drying process. The mixture was placed in an electric oven overnight (110°C) to remove residual solvent. Pellet densities before and after a dilatometry experiment are shown in Fig 6.10. Clearly addition of both the original fiber and the ball-milled fiber prohibited the microbeads from shrinking. Total shrinkage was higher for pellets with ball-milled fiber additions. The shrinkage rate of pellets with fiber addition is significantly less than that of pellets without additives in the temperature range 700-800°C, when the pellets showed the maximum shrinkage rate. Large cracks developed during heat treatment as seen on the polished cross section.

Figure 6.10: Green and final density of pellet with (A) P-100 fiber (B) Ball milled P-100 fiber additions. The pellets were processed within a dilatometer to 1500°C at a heating rate of 1°C/min
The thermosetting fiber obtained from Donac Co. was also investigated as reinforcement. Thermosetting fiber didn’t undergo a carbonization treatment. It shrinks during heat treatment and thus less stress will be generated between the fiber and carbon matrix interface. The samples were processed through the traditional powder metallurgical method by mechanical mixing of fiber and microbeads, compacting under 100MPa and sintering in the graphite furnace at 2400°C. The density of green and sintered pellets is shown in Fig 6.11. Pellets with P-100 fiber addition were prepared under the same conditions for comparison. At similar fiber length, pellets with thermosetting fiber addition gave higher shrinkage. The total shrinkage is less for pellets with longer fiber additions. Still, in all cases, the density of the heat treated pellets

![Figure 6.11: Green and final density of pellet with (◆) P-100 fiber (■) Donacarbon fiber, 130µm and (▲) Donacarbon fiber, 370µm addition. All pellets were sintered at 2400°C for 2hrs.](image_url)
decreased with an increase in fiber content. At 40wt% fiber addition, the final density is less than 1.3g/cm$^3$, significantly less than that of commercial C/C composite, which is around 1.7-1.9g/cm$^3$.

In order to increase the density of the sintered C/C composite, some of the pellets were hot pressed at various conditions. After hot pressing at 480°C for 10min under 100MPa, green density of the pellets with 40wt% P-100 fiber addition increased to 1.36 g/cm$^3$ and the final density is 1.46g/cm$^3$. Hot pressing at 200°C and 400°C has a much smaller impact on green density. Interestingly, in Chapter 4, we showed that the liquid phase formed around 450°C. Although a 30% increase in final density is achieved, it is still much less than its commercial counterpart; moreover, fairly large defects were observed on the polished cross section as shown in Fig 6.12.

Figure 6.12: Optical micrograph of pellet with 40wt% P-100 fiber addition. The pellet was hot-pressed at 480°C, 100MPa for 10min and graphitized at 2400°C for 2hrs.
6.2.3. *Al-AlN/C*

Al metal has a low melting point, 660°C. Since it is a liquid when microbead pellet has the highest shrinkage rate, Al addition won’t impede the overall shrinkage. Al reacts with carbon to form Al₄C₃, a material that is moisture sensitive. However, AlN is stable and has very good mechanical properties. The transformation of Al₄C₃ to AlN can be achieved by heat treatment in nitrogen atmosphere. The maximum processing temperature is limited as nitrogen reacts with carbon to form poisonous cyanide gas at temperatures around 1900-2000°C. Unfortunately, the transformation was not complete even after processing at 1650°C for 8hrs. All aluminum containing species transformed to AlN on the outer surface, as shown in Fig 6.13 in the surface scan profile, but a great amount of Al₄C₃ still exists within the pellet. Interestingly graphitic carbon was identified.

![Figure 6.13: XRD profile of microbeads pellets with 20wt% Al(SA) addition and processed at 1650°C, 8hrs in nitrogen flow (a) crushed powder, (b) surface scan. ▲: turbostratic carbon, ▲: graphitic carbon, ■: AlN, ◆: Al₄C₃.](image)

100
in the powder scan. Apparently the Al₄C₃ has some catalytic effect towards the formation of graphitic carbon. Submicron AlN fibers were discovered between heat-treated pellets. It could have grown from the vapor phase. The AlN formed within the pellets also has a large aspect ratio. The aspect ratio decreased as the processing temperature increased, and it almost equals to 1 when pellets were heat treated above 1600°C. As reinforcement for carbon pellets however, Al apparently is not a good choice because the small amount of untransformed Al₄C₃ will eventually lead to the disintegration of the whole pellet due to its reaction with water vapor.

Figure 6.14: Secondary electron image of AlN fiber spotted between microbeads pellets with 20wt% Al(SA) addition. The pellets were heat treated at 1400°C in nitrogen flow.
CHAPTER 7:

CONCLUSIONS

7.1. Summary of Results

This work is dedicated to the improvement of fracture properties of sintered mesocarbon microbeads. To achieve that goal, first of all, we attempted to obtain better understanding of the mechanism of carbonization by characterizing the weight loss, shrinkage behavior, off-gas composition, development of crystal structure and microstructure, etc, since it is crucial to the development of materials properties. Also, processing conditions were optimized and the effect of oxidation on the mechanical performance was investigated. Finally, reinforcements, such as milled carbon fiber, metals, borides and carbides were introduced and the effect of heat treatment temperature on materials properties was studied.

By combining the weight loss information with the gas phase composition as determined simultaneously by the thermogravimetry-mass spectroscopy, we were able to prove that the chemical processes associated with hydrogen release are responsible for the major shrinkage event. Density of the sintered pellets increased continuously with compact pressure until 100Mpa. Cracks developed during heat treatment if pellets are compacted at higher pressures. The oxidation pretreatment has several effects on the properties of mesocarbon microbeads. First of all, it introduced some acidic functional groups and improved the dispersion capability. Secondly, it increased plasticity of the
pellet and as a result effectively eliminates crack formation. However, the pellets made from oxidized microbeads shrink less during heat treatment and thus higher compact pressure is required to achieve the same density level. Thirdly, the formation of “bridges” between microbeads during the liquid phase sintering stage (<800K), critical to the development of materials properties, is inhibited due to oxidation pretreatment. Microstructural analysis indicated that a gas impermeable condition, created due to the melting of beta resin, doesn’t exist in pellets made from oxidized microbeads. X-ray analysis gave further proof as the increase in local order observed when microbeads are heat treated around 450°C, disappears after oxidation pretreatment.

In Chapter 5, TiB$_2$ was investigated as a particular reinforcement. Eutectic liquid formed when the TiB$_2$/C composites were heat treated at or above 2800K, as proved by the layered structure on the polished cross section. At low TiB$_2$ loading, liquid formation leads to homogenous distribution of TiB$_2$ in the carbon matrix with a much smaller size. The extent of graphitization and resistance to crack propagation increased. At high TiB$_2$ loading, a complete transformation of mesophase carbon to graphite is observed and fracture toughness decreased. Diffusion of TiB$_2$ to the surrounding carbon matrix initiated below the eutectic temperature. Some of the boron diffused into the carbon matrix and leads to the formation of TiC. The existence of boron in the carbon matrix is also proved and quantified by laser ablation ICS-MS. Control experiments proved that boron is not the main cause of the observed change in the material properties. Resistance of the TiB$_2$/C composite to oxidation increased due to boron oxide formation. Materials properties improved further when finer TiB$_2$ powder was used and eventually a composite with fracture toughness as high as 1.92MPa.m$^{0.5}$ was obtained, 50% higher
than that of microbead pellets processed under the same condition. It is best value reported for pressureless sintered carbon composites but less than the hot-pressed counterpart especially at high additive loadings. Average pore size decreased by one order of magnitude for the best composite.

Liquid phase formation was also found to lead dramatic property changes in the TiC/C, ZrB$_2$/C and Ni/C composites. In general pellets were found to swell during liquid phase sintering. The sintering behavior and material properties of ZrB$_2$/C are very similar to TiB$_2$/C composites. TiC catalyzed the “gradual” graphitization of mesophase carbon and leads to increased fracture properties, while catalyzed graphitization by large nickel particles only leads to the formation of graphitic carbon, and fracture toughness decreased dramatically with the increase in loading. Average pore size decreased for all pellets with improved fracture resistance, while the formation of graphitic carbon seems to be accompanied by the nucleation of large pores.

Milled carbon fiber, metals such as Al, Cu, and nitrides are found not suitable for use as reinforcement for this particular material.

It was demonstrated that high performance carbon materials can be processed from mesocarbon microbeads in a single, fast sintering step and the sintered product has better mechanical properties than traditional synthetic graphite. The fracture properties were further improved with the addition of ceramic additives such as carbides and borides through liquid phase sintering. The simplicity of materials processing, the large selection of additives available and the superior mechanical performance make the mesocarbon microbeads based carbon composites attractive material for applications such as being used as friction material.
7.2. Recommendations for Future Work

Further improvement in performance of mesocarbon microbeads based carbon composite can be achieved by the following:

1. Optimization of processing conditions. In this work, the compact pressure is selected based on the requirement to obtain pure carbon pellets with the best performance. It is not necessarily the best condition for pellets with additives, especially when the volume fraction of additive is large. The optimization of individual composition may sound impossible but it can be achieved by two methods. One way is to take advantage of liquid formation during low temperature heat treatment. We demonstrated that green density increased significantly when pellets are hot-pressed at 480°C. The ultimate way is to hot press the pellets at the sintering temperature. Tong et al. [62] and Wen et al. [64] managed to make carbon composites with extremely low porosity (<5%) through hot-pressing, which is far less than what we can achieve through pressureless sintering. The trade off is the high cost of a hot-pressing device.

2. Reduction in particle size. Smaller particle size means faster sintering and less chance of creating big pores due to liquid phase sintering. It was proved that pellets with finer TiB2 addition have a better fracture performance. Fine powder normally means higher impurity content though. Previous studies suggested that the mechanical performance should benefit from the use of finer microbeads as well.
3. Increase the beta resin content. At present the microbeads are made to produce high density carbon pellets and the beta resin content is optimized for this purpose. When foreign particles are added, more liquid is required for optimum performance as some of the melted beta resin will fill the interspaces between filler particles. Our investigation and many previous studies proved that the liquid phase sintering (<800K) is crucial to the development of materials properties.


