LIQUID FORMAITON IN CARBON COMPOSITES

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Introduction

Mesophase carbon precursor materials, either mesocarbon microbeads or mesophase pitch, have attracted attention from scientists all over the world in the past decade because of their ability to "self-sinter" into high-density carbon pellets without the help of external binder phase. A number of investigations were conducted to adjust the thermomechanical properties (Bin Hu et al. 2005; Garcia-Rosales et al. 2002).

In an effort to improve the fracture properties, the carbonization and graphitization behavior of microbeads provided by Osaka Gas Inc were studied systematically in our group. The effect of processing conditions and additives were investigated. In particular, in the study of TiB_2/C composites, we found that if the pellets were heat treated at 2800K or above, eutectic liquid forms as evidenced by the existence of a layered structure in the polished cross-section. The liquid formation was accompanied by diffusion of a small boron fraction (~1wt %) into the carbon matrix. The extent of graphitization improves dramatically when liquid forms. At high loadings and heat treatment temperatures large crystals, more than 100 microns in length, were observed on the fracture surface. A 50% increase in fracture toughness was achieved with the addition of 10vol% 10micron TiB_2 powder (Zhou et al. 2007).

In this study, the investigation was extended to several other liquid-formation capable systems, including TiC/C, ZrB_2/C and Ni/C. The experiments were designed to study the impact of eutectic liquid formation on material properties. Eutectic liquid forms at 2776ºC in the TiC/C (26.2at.%C) composite, 2390ºC in the ZrB_2/C (33at.%C) composite and 1326ºC in the Ni/C (8.9at.%C) composite.

Experimental

Mesocarbon microbeads were provided by Osaka Gas, Inc. They were manufactured from coal-tar pitch and have an average particle size around 6 microns. The nickel power (99.9% pure) was obtained from CERAC Inc and has an average size of 5 microns. TiC, Ti and ZrB_2 powers were supplied by Alfa-Aesar. They were all labeled as −325 mesh. It is claimed by the manufacturer that the ZrB_2 particles are typically less than 10 microns, and under SEM we found TiC particles are typically less than 5 microns. The powders were mixed homogeneously in a mechanical mixer (Spex 8000) and compressed into green pellets at 100Mpa. The carbonization and graphitization of the pellets were carried out in a graphite furnace in one step. The ramp rate is 1K/min at temperatures lower than 1800K and 10K/min above. The pellets were graphitized at the designated temperature for 2hrs and cooled naturally down to room temperature. The volume concentration represents the percentage of additive in the heat treated product in the final form.

The heat-treated pellets were ground into fine powders and X-ray diffraction was used to identify the phase composition. D_{002} spacing of graphite was used to quantify the extent of graphitization with silicon powder being used as internal standard.

The shrinkage behavior was characterized by using a Linseis Dual Sample Horizontal Dilatometer (Model L75HD1550). The experiments were conducted in nitrogen gas flow with a flow rate of 240ml/min.

The graphitized pellets were machined using EDM into a compact tension testing configuration and the fracture toughness was measured using ASTM E1820-01 as the guideline. The pellets were fractured in tension (Applied Test Systems, ATS 900) with a crosshead speed of 0.13mm/min. The extension of the sample during testing was monitored using an extensometer (MTS 632.12E-20).

After fracture testing, the fractured surface was observed by SEM (Model Envo6, Oxford Instruments) equipped with an EDS detector. Some of the pellets were subjected to conventional metallographic polishing and the polished surface was studied under polarized light (Olympus BX-61).

Results

TiC/C Composites

Properties of the pellets with Ti and TiC addition before and after heat treatment were shown in Table 1. At a low heat treatment temperature of 2700K, shrinkage of the pellets decreased with an increase in TiC loading. At 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 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 decreased continuously with increasing TiC volume concentration. A 52% decrease in fracture toughness was observed at 20vol% TiC addition.

Table 1. Properties of Green and Sintered Pellets with and without Ti&TiC Addition

Materials	Green Density (g/cm^3)	Final Density (g/cm^3)	Linear Shrinkage (%)	Volume Shrinkage (%)	Weight Loss (%)	Fracture Toughness (Mpa.m$^{0.5}$)	D$_{002}$ (nm)
Mcmb, pure, 2700K	1.27	1.95	16.8	42.4	11.7	1.39	0.3380
Mcmb, pure, 3073K	-	1.95	17.0*	-	-	1.24	0.3373
Mcmb, 5ol%Ti, 2700K	1.35	2.05	15.9	41.4	11.0	1.22	3.3770
Mcmb, 10vol%Ti, 2700K	1.41	2.15	15.6	40.7	10.1	1.26	3.3767
Mcmb, 20ol%Ti, 2700K	1.56	2.31	14.8	38.5	8.8	1.23	3.3715
Mcmb, 5ol%Ti, 3073K	-	2.00	16.0*	-	-	1.28	0.3363
Mcmb, 10vol%Ti, 3073K	-	2.07	15.3*	-	-	1.36	0.3357
Mcmb, 20ol%Ti, 3073K	-	2.24	14.3*	-	-	1.48	0.3355
Mcmb, 5ol%TiC, 2700K	1.35	2.01	15.6	39.7	10.6	1.20	3.3763
Mcmb, 10vol%TiC, 2700K	1.44	2.05	14.4	36.7	9.7	0.87	3.3712
Mcmb, 20ol%TiC, 2700K	1.61	2.12	12.6	31.3	9.1	0.67	3.3684

*Shrinkage in Diameter

Titanium metal reacts with carbon to form TiC phase at temperatures below 1400ºC. 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 porosity level much lower. Two factors contribute to this phenomenon. First, fewer foreign particles were added to the mixture at the same final additive level. Secondly, the reaction between Ti and C may lead to increased shrinkage. 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 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 3073K. 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.

TiC acted as a catalyst for the graphitization of mesocarbon microbeads. The extent of graphitization, as indicated by the lower d$_{002}$ spacing, is higher for pellets with Ti additions at the same additive level when heat treated at the same temperature. For pellets with 20vol% Ti addition and heat treated above the eutectic liquid formation temperature at 3073K, the d$_{002}$ spacing, 0.3355, is very close to d$_{002}$ spacing of natural graphite, which is 0.3354. Some large graphite crystals were observed on the fracture surface. The diffusion of TiC to the surrounding carbon matrix was observed at 2700K, and leads to a homogenous distribution of much smaller TiC particles, in the composite at 5vol% Ti loading and heat-treated at 3073K. At higher loading, the particle sizes seen in the polished cross sections become much larger.

Table 2. Properties of Green and Sintered Pellets with and without ZrB$_2$ Addition

Materials	Green Density (g/cm^3)	Final Density (g/cm^3)	Linear Shrinkage (%)	Volume Shrinkage (%)	Weight Loss (%)	Fracture Toughness (Mpa.m$^{0.5}$)	D$_{002}$ (nm)
Mcmb, pure, 2300K	1.27	1.92	16.2	41.4	11.5	1.53	0.3422
Mcmb, pure, 2700K	1.27	1.95	16.8	42.4	11.7	1.39	0.3380
Mcmb, 5ol%ZrB$_2$, 2300K	1.38	2.07	15.6	40.4	10.7	1.39	0.3386
Mcmb, 10vol%ZrB$_2$, 2300K	1.52	2.22	14.5	38.4	9.5	1.45	0.3381
Mcmb, 20ol%ZrB$_2$, 2300K	1.79	2.48	12.6	33.8	8.1	1.37	3.3378
Mcmb, 2.5vol%ZrB$_2$, 2700K	1.32	2.01	16.1	41.8	11.7	1.35	0.3370
Mcmb, 5vol%ZrB$_2$, 2700K	1.38	2.09	15.8	41.0	10.8	1.34	0.3368
Mcmb, 7.5vol%ZrB$_2$, 2700K	1.45	2.14	15.0	39.3	10.7	1.61	0.3365
Mcmb, 10vol%ZrB$_2$, 2700K	1.51	2.19	14.4	37.5	9.5	1.80	0.3354
Mcmb, 20vol%ZrB$_2$, 2700K	1.78	2.45	12.8	33.6	8.4	1.36	0.3352

ZrB$_2$/C Composites

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 the pellets above the eutectic liquid formation temperature at 2700K (Table 2). 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 in the same group and their chemical properties are very similar. ZrB_2 forms a eutectic liquid with carbon at very similar carbon concentration but slightly lower temperature than Ti. The development in microstructure is also very similar to what we observed in the TiB_2/C composites. For example, at a low ZrB_2 loading of 5vol%, we observed a homogeneous distribution of small ZrB_2 particles in the carbon matrix. ZrB_2 acted as a catalyst for the graphitization process. The d_{002} spacing of pellets with 20vol% ZrB_2 addition and heat treated at 2700K is less than that of natural graphite, and large graphite crystals were observed on the fractured surface.

Table 3. Properties of Green and Sintered Pellets with and without Ni Addition

Materials	Green Density (g/cm^3)	Final Density (g/cm^3)	Linear Shrinkage (%)	Volume Shrinkage (%)	Weight Loss (%)	Fracture Toughness (Mpa.m$^{0.5}$)	D$_{002}$ (nm)
Mcmb, 1700K	1. 26	1. 80	14. 3	38. 2	11. 7		0.3476
Mcmb, 5wt% Ni, 1700K	1. 31	1. 85	13. 9	36. 9	10. 5	1.27	0.3468, 0.3378
Mcmb, 20wt% Ni, 1700K	1. 45	2. 00	12. 8	33. 4	8. 4	0.77	0.3430, 0.3359

Ni/C Composites

The catalytic ability of nickel on graphitization of carbonaceous materials 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 (Otani et al. 1975). In our experiments, roughly 5 micron diameter nickel powder was used. Graphitic carbon, with d_{002} spacing around 0.336nm, was observed at temperatures as low as 900ºC. Pellets with 20wt% Ni addition were heat treated at various temperatures and it was found that a maximum fraction of graphitic carbon was achieved at 1700K. At higher temperatures, nickel extended out of the pellet, forming large particles on the outside surface, which resulted in a decreased concentration of graphitic carbon. Similar to what was observed in the TiC/C, TiB_2/C and ZrB_2/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 was shown in Figure 1. The swelling event initiates before the eutectic liquid formation temperature. Detailed experiments indicate the swelling event is observable only when pellets give the highest final densities. The experiments were terminated at several temperatures and XRD results indicate that the swelling event is accompanied by the formation of graphitic carbon phase.

Pellets with 5wt% and 20wt% Ni additions were heat treated at 1700K for 2hrs and the properties of the pellets before and after heat treatment were compared with those of pellets made from microbeads alone (Table 3). All pellets made from microbeads alone failed during machining. However, it is clear that pellets with higher Ni loading have inferior fracture properties. Almost no large graphite crystals were observed on the fractured surfaces. XRD analysis showed the formation of graphitic carbon and the catalytic ability of nickel metal toward graphitization of turbostratic carbon. The d_{002} spacing of the graphitic carbon is higher than that of natural graphite. This could be the results of defects in the catalytically formed graphite (Li et al. In press).
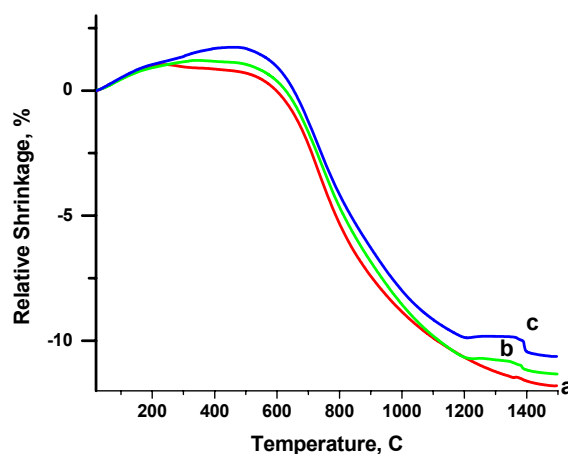

Figure 1. Shrinkage behavior of pellets made from oxidized microbeads (air, 8hrs, 150ºC) with 20wt% Ni addition and pressed at (a) 175Mpa, (b) 450Mpa, (c) 625Mpa. Nitrogen gas flow.

Discussion

The formation of liquid phase has a tremendous impact in 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 (German 1996). The phenomenon of liquid formation in carbon systems has been rarely studied. 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. Some of the interesting findings are summarized as follows:

(1) The pellets swell during the liquid phase sintering stage. 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 extensive densification (German 1996). However, recent studies on the phase transition of graphite showed that the melting process is accompanied by a large increase in volume (Savvatimskiy 2005). The swelling could be result of the local stress caused by the phase transition. Hot pressing, which is effective in eliminating porosity, should be used to increase mechanical properties.

(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 maybe related to the decreased average pore size due to the presence of the liquid phase. The variation of pore size distribution in the TiB_2/C composites with heat treatment temperature was shown in Figure 2. The average pore size decreased by one order of magnitude due to liquid formation.

(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 TiB_2/C and ZrB_2/C composites at high additive loadings when heat-treated 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 (Oya & Marsh 1982). Nonetheless, fracture properties increased at low TiB_2, TiC, and ZrB_2 loadings, although all three of the additives catalyzed the graphitization process as indicated by the decreases d_{002} spacing. Further studies on structure of the carbon materials formed under these conditions are required.
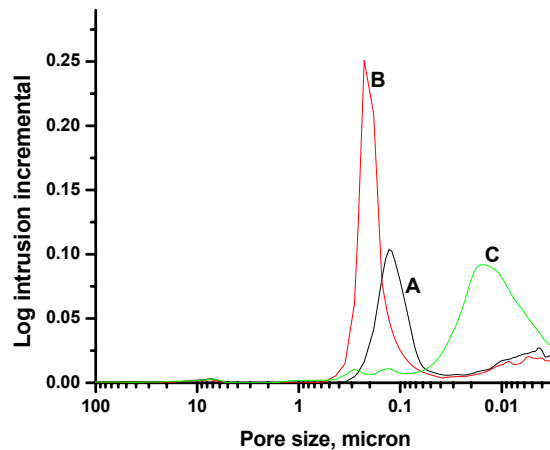

Figure 2. Pore size distribution profile of (A) microbeads pellet heat treated at 2800K, (B) pellet with 20vol% TiB_2 (10 micron) addition and heat treated at 2300K, (C) pellet with 20vol% TiB_2 (10 micron) addition and heat treated at 2800K.

Acknowledgment

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