Structural Evolution of Anthracite Coals During Reactive Ball Milling

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Introduction

Lueking et al. recently developed a combined hydrogen production and storage process through ball milling that utilized a low cost carbon precursor that slowly evolved hydrogen at room temperature [1, 2]. The evolution of the trapped hydrogen continued in excess of one year and accelerated upon mild heating. A parallel observation of nanocrystalline diamond (NCD) suggested the pathway of hydrogenative ball milling led to a hydrogenated tetrahedral carbon form that rearranged to more stable crystalline carbon forms upon heating.

The research presented here seeks to further explore the reactive ball milling process to better understand the structural transformations and the evolution of hydrogen. First, the role of thermal annealing, acid, and base treatment were explored in relation to the structural transformations that may lead to the formation of NCD with variation of metal addition during synthesis. Secondly, the precursor coal structure and the solid-solvent ratio were varied to assess the effect upon the resulting carbon material, including swelling ratio, surface area, and porosity.

Experimental

Ball milling was done on a Fritsch Planetary Mono Mill Pulverisette 6 LC – 106A with a 250 ml stainless steel vessel and stainless steel balls. Cyclohexene was used as the grinding solvent. All the samples were milled at 400 rpm in an argon atmosphere to prevent oxidation and to minimize air exposure. A total of six anthracite coals were explored in the present work, with variations in the amount of solvent addition, metal addition, and demineralization of the precursor coal. Unless otherwise specified, samples were prepared using 6 g of the solid (coal and coal with added metal) and 20 ml cyclohexene. For samples with added metal, 10% of the 6 g was either Fe powder or stainless steel powder and the remaining 90% was demineralized anthracite. After ball milling, select samples were heat treated at 1400 °C (denoted ‘HT’), treated with 4M HCl (‘A’), and subsequently treated with 10 M NaOH (‘B’).

Characterization. All samples were characterized with temperature programmed oxidation (TPO), X-ray diffraction (XRD) ultra violet Raman (UVR), and nitrogen adsorption at 77K. TPO probed the oxidative reactivity of the samples at each stage of the process, XRD probed the crystalline structures of the samples at various stages of processing, and UVR provided information on the hybridization states of the carbon forms, as well as identification of other Raman-active species present in the samples. Solvent swelling measurements were based on a method adapted from Nishioka [3,4].

Results and Discussion

Structural Transformations—Metal Addition. To explore the role of each processing step in the formation/observation of NCD, four variations in sample preparation were conducted with varying metal addition: mBMT refers to a milled Buck Mountain Coal, mDBMT refers to the coal demineralized prior to milling, mDBMT-Fe refers to a sample with added iron, and DBMT-SS refers to a sample with added stainless steel.

Figure 1 shows the TPO profiles of the different samples at each stage of processing, both with and without thermal anneal. Samples without high-temperature thermal anneal are shown as solid lines in Figure 1. BMT coal after milling (mBMT) has a maximum oxidation rate at 475 °C. Treating mBMT with HCl (mBMT-A) increases the reactivity, as is evident from the shift of the major peak (~ 475 °C) towards lower temperatures (~ 375 °C). A second peak around (~ 425 °C) suggests the presence of less-reactive carbon regions. After NaOH treatment (mBMT-AB), a third peak around 600 °C is observed, suggesting the formation of a more stable carbon frame. The residual ash content (Fig. 1, inset) is significantly reduced after acid treatment from 30.7 to 5.3%, indicating dissolution of metals by HCl (as expected). A subsequent base treatment leads to an increase in the ash content; matching the trend observed by Lueking et al. [1].

The samples with a thermal anneal (dotted lines, Fig. 1) generally oxidized at a higher temperature compared to the ones in which a thermal anneal was omitted. Specifically, the high-temperature thermal anneal shifts the TPO profile of mBMT to higher temperatures, from ~ 475 °C to ~ 510 °C. This is consistent with increased ordering of the carbon regions of the sample as well as the formation of iron carbides. The asymmetric nature of the TPO of mBMT-HT is suggestive of two types of oxidative reactivity. This shoulder present in mBMT-HT is not observed for mBMT-HT-A, indicating it is due to metal carbides. The changes in TPO after subsequent NaOH are more pronounced: the onset temperature of oxidation is significantly reduced, from 370 °C to 140 °C; such low temperatures are typically associated with amorphous carbon. Several peaks are observed in the TPO of mBMT-HT-AB, including a peak around 600 °C indicating a more oxidative-resistant carbon fraction, which was also observed for mBMT-AB. This 600 °C peak is significantly enhanced for mBMT-HT-AB when compared to the corresponding peak for mBMT-AB, suggesting the heat treatment has facilitated the formation of carbon of higher order. The thermal anneal increases the residual ash of the sample (Fig. 1, inset): to 49.6% for mBMT-HT from 30.7% for mBMT. This increase upon thermal anneal is consistent with removal of more reactive carbon fractions during the heat treatment. The trend for ash content for the ‘HT’ samples follows the same trend as that observed in the samples without the thermal anneal. However, the reduction in ash content due to acid dissolution is less pronounced after the thermal anneal (a 16.4 % decrease for thermally annealed samples vs. a 39.0 % decrease for those without thermal anneal). This is as expected for metals that become encapsulated in carbon forms during the thermal anneal.
The objective of this line of research was to determine the degree of ordering, cross-linking, or structural change that may occur during the ball milling process. Demineralized Summit (DS) and its heat treated analog (DS-HT) were chosen for these tests, as preliminary screening tests suggested that higher ordered carbons are more susceptible to being broken down during ball milling. The TPO results suggest that higher ordered carbons are more susceptible to being broken down during ball milling.

Figure 2. UV Raman spectra (244 nm) of the samples from the mBMT sequence after heat treatment, acid treatment, and NaOH treatment.

UV Raman can be instrumental in the determination of sp³ hybridized carbons. Visible Raman spectroscopy of sp² hybridized carbons gives rise to the characteristic D (defect) and G (graphite) peaks at 1350 cm⁻¹ and 1580 cm⁻¹, respectively. Diamond has a sharp D peak at 1333 cm⁻¹, but sp³ hybridized carbons such as diamond have a much smaller intensity (~1/50th) in the visible excitation compared to sp² hybridized carbons. Thus the ‘sp² shielding effect’ is reduced in UV Raman. Additionally, there tends to be a shift of the sp² D peak to higher wave numbers, helping to delineate the sp² D peak from the diamond peak. Despite these changes, recent studies by Gogotsi et al. suggest the diamond content should be more than 25% for it to be evident in UV Raman: until graphite was removed by oxidation, the characteristic diamond peak was not observed [5]. Figure 2 shows the UV Raman spectra of the AB samples from the mBMT sequence. UV Raman results for mBMT-HT-AB shows a small peak around 1331 cm⁻¹, suggestive of the presence of NCD in the sample. TEM is underway to corroborate the evidence provided by UV Raman: until graphite was removed by oxidation, the characteristic diamond peak was not observed [5].

Figure 3. TPO of DS, DS-HT and G samples with and without ball milling. Ball milled samples have been represented by solid and dotted lines represent the precursors.

Highly ordered graphite (G) had a swelling ratio value of 100% (Table 1). DS-HT has a swelling ratio of 113%, whereas DS has a swelling ratio of 124%. Thus the swelling tests confirm the expected degree of ordering (G> DS-HT>DS). Ball milling led to an increase in swelling ratio for DS-80-CH (from 124 to 150%) and for G (from 100 to 136%). DS-HT-80-CH however showed a decrease in swelling (from 113 to 100%), which likely reflects the formation of significant amounts of metal carbides for this sample (evident from TPO and XRD results, data not shown).

Table 1. Solvent swelling ratios samples DS, DS-HT and G before and after ball milling.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Swelling Ratio, before milling (%)</th>
<th>Swelling Ratio, after milling (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS</td>
<td>124 (2)*</td>
<td>150</td>
</tr>
<tr>
<td>DS-HT</td>
<td>113 (3)</td>
<td>100</td>
</tr>
<tr>
<td>G</td>
<td>100</td>
<td>136</td>
</tr>
</tbody>
</table>

*Standard deviations of multiple runs are indicated in parentheses.

Table 2: Nitrogen BET surface area and porosity results of the precursor materials. The first number is before milling, and the second number is after ball milling.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Micro-pore Volume (cm³/g)</th>
<th>Total pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS</td>
<td>4.1→326</td>
<td>0.00003→0.07</td>
<td>0.008→0.2</td>
</tr>
<tr>
<td>DS-HT</td>
<td>5.3→98</td>
<td>0.000009→0.02</td>
<td>0.008→0.2</td>
</tr>
<tr>
<td>G</td>
<td>9.4→109</td>
<td>0.000000→0.002</td>
<td>0.02→0.3</td>
</tr>
</tbody>
</table>

Ball milling leads to an increase in the nitrogen BET surface area and porosity (Table 2). The increase in surface area is ~10-fold for the ordered DS-HT and G, and ~80-fold for the less ordered DS. Ball milling significantly increased the total pore volume of the samples. Ball milling increased the pore volume for all three cases, but a more

pronounced microporosity (< 20 Å) is seen in the case of DS-80CH. The development of microporosity is in the same order as the order of the cross-linking evidenced by solvent swelling.

Conclusions
Significant structural changes were observed in the carbon fraction of milled samples at all stages of treatment: after annealing, after HCl acid treatment, and after NaOH base treatment. This was true regardless of anthracite precursor, metal addition or demineralization, and was most pronounced upon the addition of cyclohexene. Iron carbides were formed upon ball milling (XRD data, not shown). Perhaps most surprising, was the change in carbon reactivity after acid and base treatment as demonstrated by TPO. Once again, this was more pronounced in the thermally annealed samples. The BET surface area and porosity show a large increase after ball milling, and the swelling data support a greater networked, expansive structure. The presence of minerals in the precursor coal seems to be instrumental in the results. XRD and Raman results suggested the presence of sp³ hybridized regions in the mDBMT-HT-AB sample.

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References