Development of Carbon-Ceramic Composites using Fly Ash and Carbon Fibers as Reinforcement

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Abstract

Carbon-ceramic composites were fabricated by using fly ash and PANOX fibers as reinforcement. Fly ash, because of its small size particles e.g. submicron to micron level can be effectively dispersed along with fibrous reinforcements. Phenolic resin was used as carbon precursor. Both dry as well as wet methods were used for forming composites. The resulting composites were characterized for their microstructure, thermal and mechanical properties. The microstructure and mechanical properties of composites are found to be dependent on type of the fly ash, fibrous reinforcements as well as processing parameters. The addition of fly ash improves hardness and the fibers, which get co-carbonized on heat treatment, increase the flexural strength of the carbon-ceramic composites. Composites with dual reinforcement exhibit about 30-40% higher strength as compared to the composites made with single reinforcement, either with fly ash as filler or with chopped fibers.

Keywords: Fly ash, Carbon fibers, Carbon-ceramic composites, Carbothermal reduction

1. Introduction

Fly ash, a ceramic powder produced from coal based thermal power plants consists of mainly hematite, maghemite, mullite, quartz, and amorphous oxides [1]. These constituents occur mostly as spherical particles with diameter less than 25 μm. The results demonstrate that with exception of complex plerospheres, individual particles are chemically fairly homogeneous, but the pronounced compositional variation exists among particles with similar physical and structural attributes. X-ray diffraction analysis revealed that the mineralogical constituents of samples extracted from different locations are similar with respect to the phases present and differ only in the relative amounts of those phases [2]. Scanning electron microscopy revealed that fly ash contains an assemblage of carbon particles remained unburned during combustion of coal [3-5]. Magnetite particles formed from the melt which are highly porous in nature, constitute around 4-5%. The Cenospheres comprise 0.5-1.0-weight % of fly ash. This byproduct of thermal power plants with interesting properties is being utilized in various applications e.g. as a resource material for extracting various metals, magnetic particles, cenospheres etc. and as a raw material for various high temperature ceramics, acid resistant bricks, floor and wall tiles, mineral wool, sintered pozzolana aggregates, building distempers, ash alloys etc.

Newer areas of applications of fly ash are in vogue now a days. The addition of carbonaceous precursor to the fly ash can result in carbon-ceramic composite with good mechanical properties. In the present work efforts have been made to utilize the small spherical size and abrasive nature of the particle to develop carbon ceramic composite using thermosetting polymer as matrix precursor and short PANOX fibers as additional reinforcement. Since fly ash is a multioxide system in which oxides such as silica (SiO₂), alumina (Al₂O₃) and iron oxide (Fe₂O₃) are present in appreciable amount while other oxides like TiO₂, MgO, CaO, and Na₂O etc are present in small amount, it is envisaged that the addition of carbonaceous precursor to the fly ash on heat-treatment at high temperature (greater than 1450°C) can result in formation of metal carbides with good mechanical properties.

2. Experimental

2.1. Materials used

Fly ash was obtained from Thermal Power Plant, Ahmedabad, India. This fly ash was analyzed for its chemical composition, particle size distribution and surface morphology. Chemical composition of fly ash was determined through standard chemical methods. Particle size distribution of the fly ash was measured by sedimentation technique under laser using particle size analyzer PSA 2001. Surface feature and shape of the particles were observed under scanning electron microscope Hitachi S 3000N. Two-stage phenolic resin
powder with hardener obtained from Gujarat Phenolic Synthetics Pvt. Ltd. Baroda was used as carbonaceous matrix precursor. Stabilized PAN fibers were also used as reinforcement. These were characterized for their surface oxygen complexes by Boehm's titration method.

2.2. Procedure

The raw materials, viz fly ash, PAN-OX fiber and phenolic resin were mixed by using two methods, dry powder method (PR) and wet solution method (SR).

2.2.1. Dry Method

In the dry powder method, milling of the raw materials was carried out for uniform distribution of precursors in the mixture. Powder mixture was pressed in a die under 300 Kg/cm² pressure and then cured at 130ºC-150ºC temperature. Rectangular green composite blocks of size 150×30×5-7 mm were prepared. Table 1 gives details of the nomenclature and composition of different reinforcing materials and matrix in the composites used in present studies. The green composite samples were carbonized with heating rate of 30ºC/hr with dwell time of 1 hour at 1000ºC. Carbonized composites were further heat-treated at 1500ºC with heating rate of 300ºC/hr and soaking period of two hours under inert atmosphere.

2.2.2. Wet Method

Fly ash and chopped fibers were first dry mixed and then together transferred to phenolic resin/methanol solution. The mix was stirred well till thorough mixing was obtained. This mixture was oven dried at 60-65ºC to remove solvent. The dry powder mixture was pressed in a die under 300 Kg/cm² pressure and then cured at 130ºC-150ºC temperature. Rectangular green composite blocks of size 150×30×5-7 mm were prepared. These green composite samples were heat treated up to 1000ºC at heating rate of 30ºC/hr with dwell time of 1 hour under inert atmosphere.

2.3. Characterization

The samples were characterized for their physical properties e.g. density and open porosity. Open porosity was determined using kerosene infiltration method. Bulk densities were determined from geometrical dimension and mass of the samples.

2.3.1. Optical microscopy

The samples were embedded in epoxy resin and polished with SiC papers of different grade. Fine polishing was performed using alumina powder with particle size 1 μm, 0.3 μm and 0.05 μm. Polished surface was observed for the distribution of fly ash particles and fibers in the carbon matrix by using LABORLUX 12 POL S optical microscope.

2.3.2. Scanning Electron Microscopy

Surface morphology and interfacial bonding among constituents of the composites were observed in scanning electron microscope HITACHI S 3000N after coating the sample with conducting layer of Pt-Pd alloy through ion sputter Hitachi E-1010.

2.3.3. FTIR analysis

The pyrolysis of the matrix in the composite and the chemical changes occurring during heat treatment of the composites were studied on spectrophotometer SHIMADZU FTIR-8300. KBr was used as reference. The samples were mixed uniformly with KBr by keeping KBr to sample ratio 1:100. The mixture was then pulletized and analyzed by FTIR spectrophotometer.

2.3.4. X-ray Diffraction Analysis

Change in the phases during high temperature heat-treatment studies were carried out by powder X-ray diffraction technique using Philips X' Pert with Cu Ka1 (λ = 1.54056 Å) as a source.

2.3.5. Thermo Gravimetric Analysis

Thermal stability of the composites heat treated at various temperatures was studied on thermal analysis system Mettler TA 4000 with Mettler TG 50. Analysis was carried out in presence of air at heating rate of 20ºC/min up to 950ºC.

2.3.6. Flexural Strength

The flexural strength of the composites was measured on Shimadzu AG-100KN by three-point bend method. Span length to thickness ratio was kept at 16-20 and cross head

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>F910</td>
<td>Composite with 90% fly ash, 10% PF Resin</td>
</tr>
<tr>
<td>F820</td>
<td>Composite with 80% fly ash, 20% PF Resin</td>
</tr>
<tr>
<td>F811</td>
<td>Composite with 80% fly ash, 10% PF Resin, 10% oxidized PAN fibers</td>
</tr>
<tr>
<td>F730</td>
<td>Composite with 70% fly ash, 30% PF Resin</td>
</tr>
<tr>
<td>F640</td>
<td>Composite with 60% fly ash, 40% PF Resin</td>
</tr>
<tr>
<td>F631</td>
<td>Composite with 60% fly ash, 30% PF Resin, 10% oxidized PAN fibers</td>
</tr>
<tr>
<td>F622</td>
<td>Composite with 60% fly ash, 20% PF Resin, 20% oxidized PAN fibers</td>
</tr>
<tr>
<td>F541</td>
<td>Composite with 50% fly ash, 40% PF Resin, 10% oxidized PAN fibers</td>
</tr>
<tr>
<td>F522</td>
<td>Composite with 50% fly ash, 25% PF Resin, 25% oxidized PAN fibers</td>
</tr>
<tr>
<td>F423</td>
<td>Composite with 40% fly ash, 25% PF Resin, 35% oxidized PAN fibers</td>
</tr>
<tr>
<td>F424</td>
<td>Composite with 40% fly ash, 20% PF Resin, 40% oxidized PAN fibers</td>
</tr>
</tbody>
</table>
speed was 0.5 mm/min.

2.3.7. Rockwell Hardness

Rockwell Hardness of the composites was measured by digital Rockwell Hardness Tester TRSDM. Hardness measurement of composites heat-treated at 1000°C was done using ¼ in steel ball indenter by applying primary load of 10 kg then 60 kg, the value known as HRL value. Hardness measurement of composites heat-treated at 1500°C was done using ½ in steel ball indenter by applying primary load of 10 kg with subsequent application of 60 kg load, the value are thus known as HRR value.

3. Results and Discussion

3.1. Characteristics of reinforcing materials

Specific gravity of the Fly ash is 2.19 and its chemical compositions are given in Table 2. Total weight percent of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ is 86.87% therefore according to ASTM C 618 this fly ash is of class F type. Particle size distribution is given in Fig. 1, which shows that the maximum portion of the particles is of size lower than 10 microns. As evident from the SEM micrograph (shown in Fig. 2) the fly ash particles are predominantly of spherical shape. Others are fragments and lumpish particles. Carbon yield of the two stage phenolic resin is 61.47%. Surface oxygen complexes on PANOX fibers are given in Table 3. These are compared with surface oxygen complexes on carbon fibers. Hydroxyl groups, carboxylic groups and lactonic groups are in higher amount in oxidized PAN fibers as compared to PAN based carbon fibers. Thus, oxidized PAN fibers are more useful for the bonding in composites.

3.2. Physical Properties of composites

Physical characteristics of the composites prepared through solution route (SR) and powder route (PR) heat-treated at 1000°C are shown in Fig. 3. Fig. 3a shows that the densities of composites prepared through solution method are lower than that of the composites made by dry powder method. Open porosity in composites prepared through solution method is found to be higher than that of the composites made through powder route (PR). As the amount of phenolic resin increases, the densities increase and open porosity decreases in both the cases. The porosity of the composite is known to affect the mechanical strength. Therefore in order to have composites having lower porosity, high density and high mechanical strength, the composites prepared through the dry method alone were taken for further studies at high temperature heat treatment at 1500°C. It was predicted that the formation of metal carbides may improve the physical properties of the composites but detrimental reaction of the carbon matrix with metal oxides resulted in the porous carbide composite. Thus as shown in the Fig. 3b open porosities of the composites heat-treated at 1500°C are higher than those of the composites heat-treated at 1000°C and hence it gives poor mechanical properties.

3.3. FTIR spectroscopy

![Carbon particles](image)

Fig. 2. SEM micrograph of fly ash.

**Table 2. Chemical composition of fly ash**

<table>
<thead>
<tr>
<th>Metal Oxides</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>TiO$_2$</th>
<th>CaO</th>
<th>MgO</th>
<th>K$_2$O</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Weight</td>
<td>56.34</td>
<td>22.63</td>
<td>7.9</td>
<td>1.84</td>
<td>2.89</td>
<td>1.28</td>
<td>1.5</td>
<td>2.86</td>
</tr>
</tbody>
</table>

![Particle size distribution in fly ash](image)

Fig. 1. Particle size distribution in fly ash.

**Table 3. Surface oxygen complexes of the fibers**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\text{-OH}$ (meq/100 gm)</th>
<th>$\text{-COOH}$ (meq/100 gm)</th>
<th>Lactonic (meq/100 gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN-OX fibers</td>
<td>405</td>
<td>361</td>
<td>84</td>
</tr>
<tr>
<td>PAN based Carbon fibers</td>
<td>60</td>
<td>57</td>
<td>60</td>
</tr>
</tbody>
</table>
FTIR spectra of the composites heat-treated at different temperatures are shown in Fig. 4. It show peaks at 1100 cm$^{-1}$~1200 cm$^{-1}$ and 500 cm$^{-1}$~600 cm$^{-1}$ attributed to Si-O stretching and alluminosilicates respectively. C=N stretching at 1591.2 cm$^{-1}$ was observed in milled powder due to acrylic fibers. Peak at 1506.3 cm$^{-1}$ reveals the C-O stretching. Along with the Si-O stretching and alluminosilicate, the composite heat treated at 1000°C show absorption at 1706 cm$^{-1}$ due to presence of carbonyl groups. No peak for C=N stretching was observed in heat-treated composites. Additional peak at 854.4 cm$^{-1}$ was observed for the Si-C stretching. These results indicate the formation of silicon carbide during carbothermal reduction.

3.4. Surface Morphology

Fig. 5 shows SEM micrographs of as mixed raw materials. Fig. 5a shows the fly ash particles alone well covered with resin particles. Fig. 5b shows uniform distribution of particles of milled powder and the fibers well covered with the resin particles.

The optical micrographs of the composites HTT 1000°C are shown in Fig. 6. These also show uniform distribution of the fly ash particles in the glassy carbon matrix. Optical
activity is observed at the interface between fly ash particles and carbon matrix, revealing anisotropic behaviour in the carbon matrix. The presence of oxides of Iron e.g. hematite and magnetite in the fly ash contribute to the anisotropy in the matrix at the interface between glassy carbon and surface of the particles [6].

Fig. 7 shows SEM micrographs of the composites made with fly ash and fibers after HTT at 1000°C. These show uniform distribution of reinforcements in glassy carbon matrix. A comparison of micrographs of the reinforcing materials (Fig. 5) and of the composites heat-treated at 1000°C (Fig. 7a) reveal not much change in the shape of crystalline particles. But it appears that on heat-treatment at 1000°C, formation of partial liquid phase due to dissolution of glassy particles takes place (Fig. 7b). At higher temperature, sintering results in neck growth between micro sized particles as the liquid phase formation and viscous flow sintering took place within fly ash particles [7].

Adhesion between fly ash particles and carbon matrix and cohesive bonding between fly ash particles themselves contribute to the strength of the composite at 1000°C. A liquid phase sintering produces mullite grains in comparatively very low amount and these are confirmed through XRD. A comparison with the equilibrium phase diagram of the $\text{Al}_2\text{O}_3-\text{SiO}_2$ system reveals the formation of liquid phase at substantially higher temperature range from 1550°C to 1850°C (8). Comparing this with present results suggests that the presence of the alkali metal oxides in fly ash shifts the pseudo eutectic point to a lower temperature [8].

Fig. 8 shows spherical fly ash particles getting converted into beautiful polyhedral geometry during reaction at high temperature (1500°C).

3.5. X-ray Diffraction

Fig. 9a shows XRD spectra of different composites HTT at 1500°C. It shows characteristic peaks of $\beta$-SiC having 2$\theta$ values as 35.63°, 60.04°, and 71.82°. Characteristic peaks of free carbon were not observed in composites containing 60%
fly ash and 40% phenolic resin due to carbothermal reduction reactions. Fig. 9b shows the diffractogram of the composites containing 60% fly ash 20% phenolic resin and 20% fibers HTT 1500°C. The characteristic peak of free carbon was observed at 26.26° along with characteristic peaks of β-SiC indicating presence of substantial amount of carbon after carbothermal reduction. This peak was predominantly from the fibers which get co-carbonized and oriented when heat treated to 1500°C. The XRD of reduced oxides shows the presence of additional three peaks of iron carbides (Fe₂C) at angles 37.4° (2.40 Å), 45.20° (2.04 Å) and 49.24° (1.84 Å). Presence of quartz and mullite phases was also observed in the composites heat-treated at 1500°C. XRD data shows that two kinds of phenomena are appearing to be taking place simultaneously. One is reaction sintering of silica and alumina above 1200°C and second carbothermal reduction of metal oxides e.g. SiO₂, Fe₂O₃ etc. with carbon to produce metal carbides.

3.6. Thermo Gravimetric Analysis

Fig. 10 shows TGA curves of the composites heat-treated at 1000°C and 1500°C in air. The composite heat-treated at 1000°C show onset of weight loss at 200°C while composite fired at 1500°C show onset of weight loss at 650°C. Weight loss in composites heat-treated at 1000°C is due to oxidation.
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of carbon matrix while in composite heat-treated at 1500°C, it gets converted to carbides which have better thermal stability and oxidation resistance.

3.7. Mechanical properties of the composites

Fig. 11 shows flexural strength of carbon-ceramic composites made with various compositions. As the weight percentage of the fibers increases, there is an increase in the strength of the composites. As the fiber percentage increases from 20-25% the breaking load increases by 100% and flexural strength get increased by 71.05%. When the weight percentage of the fiber increase from 25-40% the breaking load increases by 50% and flexural strength get increased by 35.12%.

The results of Rockwell Hardness of the carbon-fly ash composites made with various compositions are given in Table 4. It shows that the hardness of composites heat-treated at 1000°C decreases as the amount of fly ash increases. Composites heat-treated at 1500°C also show opposite trend, i.e. an increase in hardness on addition of fly ash. However, the percentage increase in strength of the composites when heat-treated from 1000°C to 1500°C decreases with increase in fly ash content. In fibrous composite, the hardness is more than that of the composite without fibers at 1000°C. At high temperature, a decrease in hardness is observed. The decrease in hardness of the composites (HTT1500°C) may be due to increase in porosity.

4. Conclusions

The carbon ceramic composites having desired mechanical properties can be obtained by using fly ash and carbon fibers as reinforcements in carbon matrix. Both get distributed uniformly and well bonded with carbonaceous polymeric precursor, and hence it gives composite with good mechanical properties on heat-treatment at 1000°C. Heat-treatment at 1500°C results in carbothermic reduction producing metal carbides like SiC and Fe₂C. The carbothermic reduction also results in formation of pores in the composites that reduce hardness. Addition of fibrous reinforcement increases flexural strength, but the hardness of the composites heat-treated at 1500°C decreases as the amount of fly ash increase or fibrous reinforcement decreases. In case of composites heat-treated at 1500°C, the hardness increases on increasing amount of fly ash, may be due to the formation of metal carbides.

Acknowledgement

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References