Tailoring of density in carbon foams

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Received 15 January 2008; accepted 31 October 2008

Cell-size of the sacrificial polymeric scaffolding and concentration of the impregnating phenolic resin are taken as two variables for tailoring density in the carbon foam. Effects of cell-size and resin-concentration on density of carbon foam are studied under three categories: (i) individual effect of varying cell-size with fixed resin-concentration, (ii) individual effect of varying resin-concentration with fixed cell-size, and (iii) synergistic effect of varying cell-size and resin-concentration. For a fixed resin-concentration and particularly for lower concentration of 10%, density marks a small incremental effect with the reduction in cell-size. It increases from 0.041 to 0.055 g/cc for a cell-size of 30 PPI (pores per inch) and 80 PPI respectively. For a fixed cell-size and particularly for lower cell-size of 80 PPI, density shows a large incremental effect with increase in resin-concentration. Density increases from 0.055 to 0.210 g/cc for a resin-concentration of 10% and 90% respectively. Under the combined effect of decreasing cell-size and increasing resin-concentration, density records a massive increase of 412.2% from initial combination of 30 PPI cell-size and 10% resin-concentration to last combination of 80 PPI cell-size and 90% resin-concentration.

Foams, the cellular material, can be designed to meet a complex and conflicting set of requirements involving stiffness, strength, thermal conductivity, surface area and gas permeability. During past few years, a variety of refractory-metal and ceramic foams have been developed mainly for high temperature applications1-3. Carbonaceous foams, belonging to this category, can be used up to temperatures as high as 2500°C. Attractive properties of these foams include ultra low density, low thermal expansion, high chemical purity and very good thermal stability coupled with excellent thermal shock resistance. They also provide possibility of being processed in near-net shapes. This impressive combination of properties makes the carbon foams suitable for many aerospace and industrial applications, which include the thermal protection of reentry/reusable space vehicles4,5, shock absorption, catalyst support, metal and gas filtration and also as a substrate for depositing layers of refractory materials by CVD/CVI technique.

Density of carbon foams is one of the critical governing criteria in the selection of this material particularly for aerospace applications. Moreover, density is the most important parameter which affects the mechanical behaviour of foams. Several techniques which are reported to process carbon foams including syntactic foams based on carbon microballoons6, foaming of mesophase pitch7, deposition of polymide film on foam templates8 and porous carbon using zeolite as template9, enable only coarse control of the density in foamed structures. In this paper, we present a process-mechanism which allows coarse as well as fine control of density of carbon foam while maintaining the uniformity and pore-interconnectivity of the inherited reticulated structure of the foam.

Experimental Procedure

Process-mechanism evolved by us for synthesizing the carbon foams is based on the use of a thermodegradable or sacrificial scaffolding which is impregnated by a polymeric resin. Resol type phenolic resin was used for impregnation purpose. Various combinations of cell size of the sacrificial polyurethane foam scaffolding and concentration of the impregnating resin employed in the present work are given in Fig. 1. The matrix contains entire range of possible combinations between the five sets of cell-size and resin-concentration each. Five sets of cell-size represent the viable options available for impregnation purpose. Impregnation becomes ineffective below the cell-size of 80 PPI. Five variants of resin-concentration represent incremental values optimally suited for the present studies. Organic solvent based on the hydroxyl group was used as
diluting regent for controlling concentration of the resin. Special care was taken to drain out excess resin from the porous scaffolding or substrate to avoid blockage of cells. The resin enriched substrates were dried in natural environment under monitored conditions. This imparted sufficient rigidity and therefore enabled safe handling of the foamed structure for subsequent thermosetting operation which was carried out at 150°C for two hours in an air oven. Selected samples were subjected to progressive processing for pyrolysis (at 450°C) and carbonization (at 1000°C and 1900°C) under high purity inert gas atmosphere.

Density of carbon foam samples representing all the combinations of cell-size and resin-concentration, was measured under thermoset state. Flatness of the opposite circular surfaces of cylindrical specimen was ensured before taking measurements. Average of two geometrically orthogonal diameters and average of corresponding heights was considered for calculation of volume of the cylindrical samples. Electronic balance with accuracy up to ± 0.01 g was used for measuring weight of the specimens. SEM observations were made using Phillips’ XL30 Model microscope mainly to study morphological features of the individual struts in the foamed structure. FTIR analysis of the specimens from various stages of processing was carried out in the spectral range of 4000-400 wave number employing Perkin Elmer Spectrum GXA Spectrometer.

**Results and Discussion**

Before presentation and analysis of results of this study, an understanding of morphology of the foamed structure is very essential. In our experiments, we dealt with reticulated foams with entirely open cell structure. Cells were made of three-dimensional interconnected network of struts (Fig. 2). Width and length of the strut are a function of cell-size. The larger is the cell size, the higher are the values of width and thickness of the strut. Gibson and Ashby model\(^1\) stipulates a linear relationship between thickness and length of the strut. The model also describes the mechanical behaviour of a foam in terms of these strut dimensions which are also related to relative density.

For tailoring density of the foamed structure, we selected two variables. These variables are based on
the raw material parameters namely cell-size of the substrate foam and concentration of the impregnating resin. As shown in Fig. 3, the general effect of these two parameters on density is that density increases with: (i) increase in resin-concentration and (ii) decrease in cell-size of the substrate foam. Minimum density of 0.041 g/cc and maximum density of 0.210 g/cc are achieved with the following two combinations of resin-concentration and cell-size: 10%-30PPI and 90%-80PPI respectively. Another trend, which is discernible from Fig. 3 is that lower resin-concentrations in combination with higher cell-sizes enable subtle control of density within a narrow range. On the other hand, achievable density-ranges become broader with higher resin-concentration and lower cell-size combinations.

The mechanism of density build-up in these foams is based on absorption of resin by struts of the substrate foam. As shown in Fig. 4 struts of the substrate polyurethane foam are made of a highly porous structure consisting of both micro and macro pores. Density of undiluted resin (1.3 g/cc) is about 42 and 37 times higher than density of 30 PPI (0.031 g/cc) and 80 PPI (0.035 g/cc) substrate foams respectively. Highly porous struts when absorb higher density resin, it results into density build-up in the resultant foam. The amount of resin absorbed by the struts is mainly a function of surface-area of struts in unit area/volume of the substrate foam. This, in turn, depends upon the number of cells present in the unit area/volume of foam. Table 1 gives this number for the five types of the substrate foams used by us. For the purpose of calculation, the cells are taken as circular in cross-section and cell-size given in the Table 1 is taken as diameter of the cell. As evident from Table 1, number of cells present in unit area increases with decrease in cell-size. Therefore, substrate foams of small cell-size have more surface area of struts available for the absorption of resin. This results in progressive build-up of density in resin impregnated foams with decrease in their cell-size. The effect of resin-concentration on density build-up in foam is due to increase in density of resin with increase in its concentration. Therefore, absorption of denser resin by struts leads to higher density of the resultant impregnated foams.

Further analysis of the effect of resin-concentration and cell-size on density of carbon foam, can be done under three categories: (i) individual effect of varying cell-size with fixed resin-concentration, (ii) individual effect of varying resin-concentration with fixed cell-size, and (iii) synergistic effect of varying cell-size and resin-concentration. For a fixed resin-concentration, density marks smaller incremental effect with the reduction in cell-size. This incremental effect is particularly very small for lower

<table>
<thead>
<tr>
<th>Type of substrate foam</th>
<th>Cell-size (mm)</th>
<th>Cells per unit area or in one mm²</th>
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<tbody>
<tr>
<td>30 PPI</td>
<td>0.82</td>
<td>1.9</td>
</tr>
<tr>
<td>40 PPI</td>
<td>0.61</td>
<td>3.4</td>
</tr>
<tr>
<td>50 PPI</td>
<td>0.49</td>
<td>5.2</td>
</tr>
<tr>
<td>60 PPI</td>
<td>0.41</td>
<td>7.7</td>
</tr>
<tr>
<td>80 PPI</td>
<td>0.31</td>
<td>13.3</td>
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</table>
values of resin-concentrations. To illustrate this observation, variation in density for 10% resin-concentration is shown Fig. 5. For this concentration, density increases only by 34.1% from 30 PPI to 80 PPI cell-size. However, for fixed cell-size, density marks larger incremental effect with increase in resin concentration. This incremental effect is particularly very large for lower cell-sizes. As illustrated for 80 PPI cell-size in Fig. 6, density registers a big increase of 281.8% for variation in resin-concentration from 10% to 90%. Effect of resin-concentration on strut morphology is depicted in Fig. 7. Struts appear studier and thicker when they absorb resin of higher concentration.

Synergistic incremental effect of decreasing cell-size and increasing resin-concentration on foam density is shown in Fig. 8. It is synergistic because reduction in cell-size alone imparts maximum 34.1% increase in density (Fig. 5), while increase in resin-concentration alone results in maximum 281.8% increase in foam density (Fig. 6). However, as evident from Fig. 8, density under the combined effect records a massive increase of 412.2% from the initial combination of the 30 PPI cell-size and 10% resin-concentration to the last combination of 80 PPI cell-size and 90% resin-concentration. Thus, combined effect of decreasing the cell-size and increasing the resin-concentration on enhancing the foam density, is much more pronounced than the individual effects of decreasing cell-size and increasing resin-concentration.

For tailoring density in carbon foams, we employed high char yielding phenolic resin. Concentration of resin was varied by adding diluting organic solvent based on hydroxyl group. During subsequent thermosetting operation of resin impregnated substrate foams at 150°C, this solvent got completely removed as volatiles from the foamed samples. To assess the effectiveness of this process on the integrity of the subsequent carbon foam structure, few thermoset foam specimens were subjected to pyrolysis (450°C) and carbonization (1000°C and 1900°C) treatments. Results of FTIR analysis of these samples are given in Fig. 9.

As revealed by Fig. 9, specimen treated at 1900°C does not show the presence of any functional group. This, in turn, confirms the constitution of the foamed structure entirely by carbon and establishes effectiveness of the process evolved in the present study. Visual and SEM observations of the processed carbon foam delineate a completely reticulated structure constituted by a well interconnected network.
Conclusions

Concentration of the phenolic resin in combination with cell-size of the substrate foam provides an effective method for tailoring density in carbon foam. Lower resin concentrations enable a fine control of the resultant density. Coarse control of density is facilitated by the small cell-sizes. Combinations of increasing resin-concentrations and smaller cell-size have synergistic incremental impact on the density. The evolved process yields completely reticulated carbon foam constituted by well interconnected network of struts.

Acknowledgement

We thankfully acknowledge the support of Materials Characterization Division and Analytical and Spectroscopy Division of VSSC for this research activity and permission granted by Director, VSSC for publishing the work.

References