Lightweight vitreous carbon material: approaches to making open-pore cellular structure

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Abstract: *Cellular vitreous carbons with the open-pore structure are attractive materials in some aerospace applications, such as the super-lightweight structural materials or sandwich core materials in the thermal protection systems. Cellular vitreous carbon (or VC foam) with the open-pore structure can be synthesized by pyrolysis of cellular precursor structures made from some types of resins, such as epoxy or phenolic resins. Several approaches elaborated at RPMI, Belarus can be applied to create the precursor resin foams. The replication approach ensures perfect open-pore structure with the porosity of >90% and high hydraulic permeability. The sacrificial template approach ensures lower porosity and hydraulic permeability, and higher specific strength. In the approach with the deformable space-holder granules in the sacrificial template, the foam porosity can be controlled in a wider range. The paper compares different methods of making the precursor resin foams and properties of VC structures synthesized by pyrolysis of these precursor foams.*

Key Words: *vitreous carbon, open-pore foam, replication approach, sacrificial template approach*

1. INTRODUCTION

Cellular vitreous carbons with the open-pore structure (VC foams) are attractive materials in some aerospace applications, such as the super-lightweight structural materials or sandwich core materials in thermal protection systems [1, 2]. This is due to an advantageous combination of thermo-physical and specific mechanical properties, low density and high operating temperatures. Thus, VC foams can operate at temperatures as high as above 2000°C in anoxic environments, and their density can be as low as 0.05-0.03g/cm^3. The open-pore structure of VC foams is very important in the applications mentioned above; this permeable structure ensures circulation of cooling media within the sandwich core and is not sensitive to exploitation under the vacuum or decompression conditions.

The open-pore VC foams can be synthesized by the pyrolysis of the preliminarily prepared precursor foams made from some types of resins, such as phenolic resin, epoxy resin, or furfuryl alcohol [3-10]. The pyrolysis is carried out in the inert gas flow (argon, nitrogen) at temperatures of >1000ºC.

As a result, the resins are converted to carbon whereas the original cellular structure of the precursor foam remains unchanged, just undergoing certain volumetric changes. Carbon that is synthesized during pyrolysis has a disordered crystal structure with a not regular orientation between the graphite-like hexagonal layers. This carbon type is known in the literature as vitreous or glassy carbon.

The vitreous carbon attracts designers of structural components because it has low density (2/3 of the graphite theoretical density) and superior mechanical properties as compared to the same of graphite [3].

Thus, preparation of a precursor foam with the targeted cellular structure from a pyrolyzable resin is the key component of the VC foam synthesis process. The most widespread preparation process of the precursor resin foams is based on the replication approach in which structural elements (struts) of the reticulated polyurethane foam template are covered with a thin resin layer.

After setting the resin, the open-pore cellular structure can be immediately pyrolyzed [5-9]. The VC foams synthesized by this method are also known as reticulated vitreous carbon (RVC) foams because they have typical reticulated foam structure consisting of the interconnected polyhedral cells.

All classical precursor resin types can be used in this method. Another approach ensuring an open-pore cellular structure is based on the sacrificial template approach in which a template is made as a bed of the densely packed granules that can be impregnated with a precursor resin [4, 10]. After setting the resin, the template is leached away, and the resultant cellular structure can be pyrolyzed. In this method, epoxy resin is the preferable precursor because it usually does not require adding volatile solvents that are difficult to evacuate from the template depth.

Both the replication and sacrificial template approaches were studied at RPMI [4, 5]. The VC foams are suitable for sandwich composite systems used especially in the aerospace industry. The CFRP faces are the latest trend in structural sandwich system with foam core [11]. The main advantage of the sandwich structure is that its properties can be adjusted in accordance with technical requirements by choosing the component materials. The purpose of this paper is to explain the features of cellular structures made by different methods and how the method affects properties of resultant VC foams.

2. APPROACHES TO MAKE PRECURSOR CELLULAR STRUCTURES ELABORATED AT RPMI

The replication method elaborated at RPMI comprises multiple impregnations of the reticulated polyurethane foam (PUF) plate with the ethanolic solution of bakelite that is the thermosetting phenol-formaldehyde resin.

For this, the PUF plate with the required cell size is immersed into the bakelite solution and then centrifuged to remove the excess solution. As a result, a thin bakelite layer is retained on the PUF struts; the layer thickness can be controlled through the variation of the bakelite solution concentration. Then, after drying and setting bakelite, the impregnation can be repeated to increase the layer thickness. The process is described in detail in Ref. [5]. The main advantage of the elaborated process is that the precursor foam density can be precisely

controlled by the number of impregnations; the really achieved density range was 0.07-0.35 g/cm^3. The resultant VC foam structure achieved after pyrolysis of this precursor resin foam and its virtual cross-section are presented in Fig. 1(a). The porous structure consists of fully open interconnected cells in which the structural elements (struts) are the edges of closely packed polyhedrons.

In the sacrificial template approach, the precursor resin fills the free space in the bed of leachable granules thus forming a 3D cellular skeleton, i.e. a foam-like cellular structure is formed due to the structure inversion [12].

The preparation method of the precursor resin foam is described in detail in Ref. [4]. In this method, spherical carbamide granules are moistured with the ethanolic solution of polyvinyl-pyrrolidone, packed in a mold and dried. Thus, a rigid template is formed, adjacent granules in the template are connected with the polyvinyl-pyrrolidone necks. Then epoxy resin mixed with a setting catalyst is infiltrated into the carbamide template, and, after setting the resin, the template is leached out in water.

The precursor foam can be pyrolyzed after drying; the image of the resultant cellular structure and its schematic image are given in Fig. 1(b). The structure is formed as a system of the closely-packed spherical cells with interconnecting round windows. The limitation of this method is that the density of the precursor resin foam cannot be controlled in a wide range and is usually within 0.36-0.40 g/cm^3.

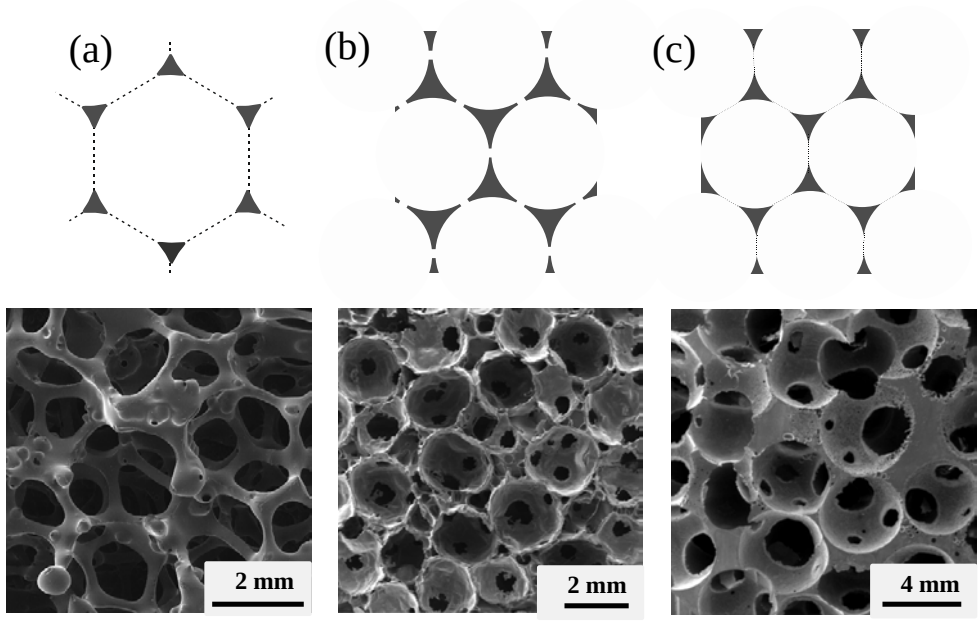

Fig. 1 – Open-pore VC foam structures made by different methods: (a) replication of PUF structure; (b) sacrificial template method with non-deformable space-holder granules; (c) sacrificial template method with deformable space-holder granules

In order to eliminate this limitation, a modified method, not reported before, was studied. In this method, the sacrificial template is made from the expanded polystyrene granules. The bed can be easily deformed by compression, which is the tool for controlling free space between granules in the template.

It was stated experimentally that the expanded polystyrene granules retain near-spherical shape at the template's relative deformation at compression of less than 50%. At such deformations, the polystyrene granules are subjected to deformation mostly at contacting

areas, and the inter-granular space forms a continuous 3D network that can be filled with the precursor resin. Epoxy resin mixed with a setting catalyst can be infiltrated into the deformed polystyrene template, and, after setting the resin, can be leached out in organic solvents (benzene, acetone, or xylene). Cellular structure achieved after pyrolysis of this precursor resin foam is presented in Fig. 1(c).

As compared to the sacrificial template method with the template made from non-deformable granules, this one ensures the larger controllable range of the precursor resin foam density (0.15-0.30 g/cm^3) as well as larger variation in the window size between adjacent cells.

The ranges of VC foam relative densities that can be achieved with different precursor resin foam preparation methods are summarized in Fig. 2.

It should be noted that the apparent densities of the VC foams are different from the same of the precursor resin foams because of the combination of phenomena taking place at pyrolysis, such as linear shrinkage at pyrolysis (>20%), remarkable weight losses due to decomposition of the resin precursors (~50%), the density decrease of the structure-forming material (to 1.45-1.5 g/cm^3 in our experiments) and the formation of the micro- and nano-scale porosity. The apparent density of the synthesized VC foams ranged within 0.06-0.25 g/cm^3 in the processes described above.

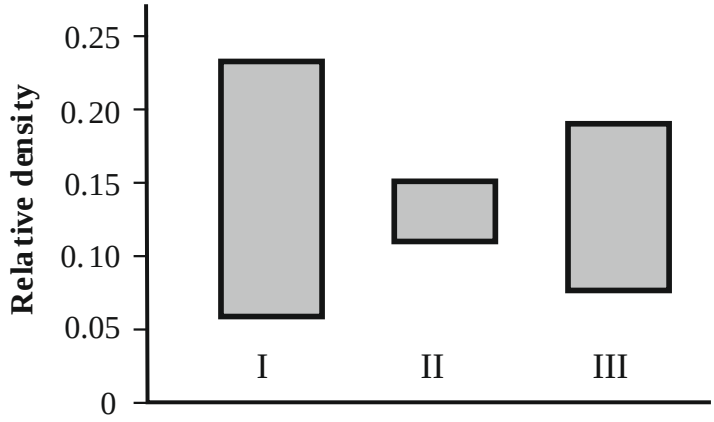

Fig. 2 – Relative density of VC foams structures made by different methods: (I) replication of PUF structure; (II) sacrificial template method with non-deformable space-holder layer; (III) sacrificial template method with deformable space-holder layer

3. PROPERTIES OF VC FOAMS MADE BY DIFFERENT METHODS

As it was explained in the previous section, different precursor resins were applied in different methods. The replication approach was stated to be applicable for different precursor resin types. In the sacrificial template approach, the use of precursor resins containing volatile solvents is objectionable because the release of the solvents from the template volume is hindered, hence, they can be the source of the microstructure defects. That is why epoxy resin was only considered as the precursor in this method. Both precursor resins applied in the studies were successfully converted into vitreous carbon; similar XRD patterns were received after pyrolysis at 1100^{o}C in the nitrogen flow (Fig. 3). The analysis of the peak positions and the broadening of reflections showed that in both cases the spacing between the hexagonal layer planes increased remarkably as compared to graphite, and the crystalline size (the coherent length) was ~20-40 nm [5].

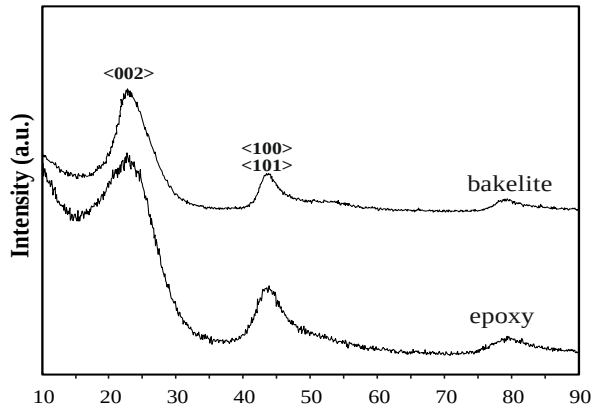

Fig. 3 – XRD patterns of vitreous carbons received by pyrolysis of bakelite and epoxy resin

As for mechanical properties and hydraulic permeability of the VC foams, the precursor foam preparation approach had a remarkable effect.

The dependencies of the specific strength at compression vs relative density of VC foams made via the replication and the sacrificial template approaches are shown in Fig. 4. As can be seen, the sacrificial template approach could ensure higher specific strength at the same relative density in all the studied range, and the strength increase with the density increase was more intensive. This is defined by features of cellular structures received by the different method. VC foams made by the replication method have the classical reticulated structure in which the dependence of compressive strength on relative density is well described by the power law with the exponent equal to 1.5. In the other foam type, the structure is similar to the same of classical closed-cell foams in which the strength evolution is described by a more complex law that is closer to the linear dependence [13]. The expected dependencies that were estimated using the model equations are given as the dashed lines in Fig. 4.

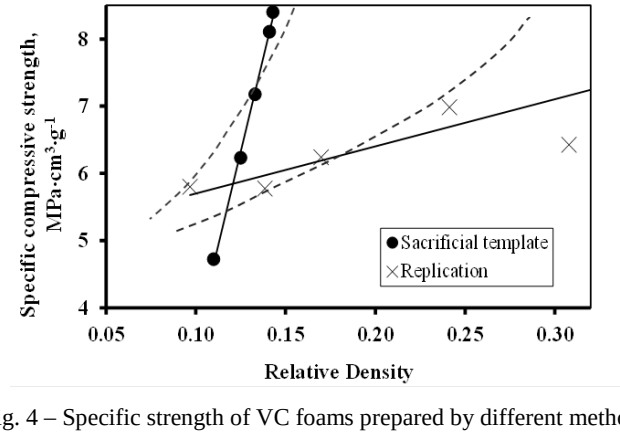

Fig. 4 – Specific strength of VC foams prepared by different methods

The deviations from the experimental data are defined by the structural changes depending on the relative density, such as coalescence of neighboring windows between cells at low relative densities in the sacrificial template method and bubbling the foam struts at high relative densities in the replication method [4, 5]. As a whole, both manufacturing approaches ensured VC foams with the compressive strength of 0.5-2.5 MPa, but higher specific strength values could be achieved with the sacrificial template method.

The hydraulic permeability coefficients of the VC foams made by the replication and the sacrificial template methods are shown in Fig. 5. The foams had the average cell diameters of ~3-4 mm in both cases.

It can be seen that VC foams made by the sacrificial template method had evidently higher hydraulic losses.

This must be attributed to the smaller window size / cell size ratio and, consequently, a larger contribution of hydraulic losses due to compression and expansion at passing air through the cellular structure.

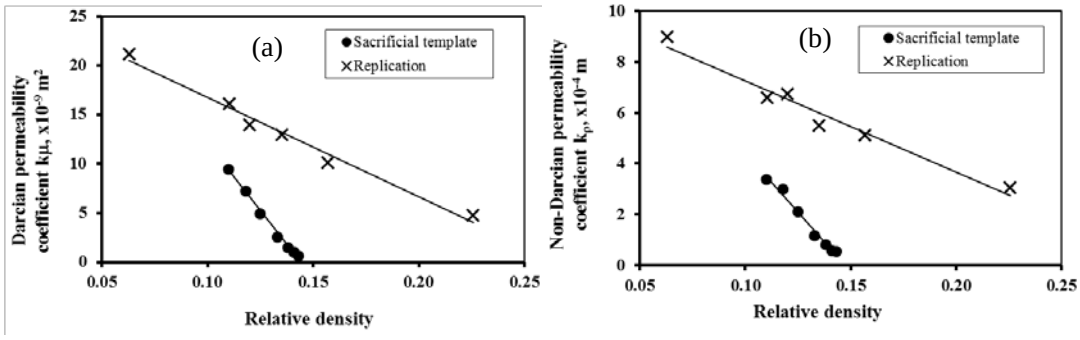

Fig. 5 – Darcian (a) and non-Darcian (b) permeability coefficients of foams made by different methods

Thus, the comparative analysis of mechanical and hydraulic properties of VC foams showed that the foams manufactured by different methods can be more or less attractive for different targeted applications.

If the precursor resin foam is made by replication of the polyurethane foam template, the final VC foam would be more attractive in applications where hydraulic permeability is the limiting property.

If the precursor resin foam is made by the sacrificial template method, the resultant VC foam would be better used in applications requiring the improved strength-to-weight ratio.

4. CONCLUSIONS

Different approaches were studied to prepare the precursor resin foams for the subsequent synthesis of the vitreous carbon foams by pyrolysis in an inert atmosphere. Independently on the approach and the precursor resin applied, the resins were converted into vitreous carbon with the strongly disordered hexagonal lattice.

All the studied approaches ensured cellular permeable structures with low density and high specific strength. Depending on the targeted application, different exploitation parameters (hydraulic permeability, strength) can be emphasized by applying different manufacturing methods and selection of the density range.

This is important for designing super-lightweight structural materials and sandwich core materials in thermal protection systems.

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