

# A SEM Record of Proteins-Derived Microcellular Silicon Carbide Foams

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**ABSTRACT:** Protein rigid foams based on albumin coreacted with camphor and an aldehyde were converted into silicon carbide (SiC) foams. This was carried out by putting albumin-derived template foams in contact with silicon compounds in liquid phase and calcinating the mix obtained at a relatively low temperature of 500°C to eliminate the protein and leave the SiC foam. The transformation was followed by scanning electron microscopy (SEM) from the natural albumin foams to the gel obtained by infiltrating them with tetraethyl orthosilicate (TEOS) and to the appearance of the SiC foams after calcination. X-ray diffraction (XRD) and Raman spectra were done to characterise the resulting foam.

**KEYWORDS:** Protein rigid foams, silicon carbide foams, scanning electron microscopy

## 1 INTRODUCTION

Microcellular foams, biosourced at a 93–95% level, have recently been developed on the basis of the reaction of tannins and furfuryl alcohol in the presence of blowing agents and without blowing agents under different sets of conditions [1–6]. These materials possess high porosity and physical properties similar to those presently found in commercial synthetic phenolic foams [1,2,6]. The formulation of these foams has been adapted to a variety of different applications such as acid and alkaline type foams [1,7] for rigid fire and thermal insulation [8], acoustic insulation [9], rigid cut flower foams and hydroponics [10], carbonized foams for several applications [11,12], and elastic flexible foams [13]. Among these applications, an approach in which microcellular silicon carbide (SiC) foams were prepared from natural tannin-furanic-based template foams was reported [14].

The interest in converting tannin/furanic foams into SiC was due to silicon carbide being a material combining excellent thermal stability, high thermal conductivity, high mechanical resistance at high temperature, low coefficient of thermal expansion, and

excellent resistance to thermal shocks and to abrasion [15,16]. This renders it particularly suitable for electrical [17], high temperature [18–21], catalyst support [22,23] and solar absorber [24,25] applications.

However, different types of biosourced microcellular foams based on different materials, namely proteins (mainly albumin), based on a different preparation technology and almost 100% naturally derived, have also been prepared and reported [13,26]. These, which are more delicate than their tannin/furanic counterpart, were also of interest for conversion into SiC. This conversion into SiC foams was carried out in the present work by putting albumin-derived template foams in contact with silicon compounds in liquid phase and calcinating the mix obtained at a relatively low temperature of 500°C. For this purpose, a different experimental approach than that used for tannin/furanic foams has been tested for the first time with these types of natural precursors.

## 2 EXPERIMENTAL

### 2.1 Preparation of the Albumin Foams

The procedure followed was [26]: 37% water solution of formaldehyde (F), camphor and water were first mixed together. After stirring, industrial powder albumin (chicken egg, SIGMA Chemical CO., and in one

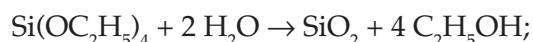
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case PROLABO albumin) was added, followed by stirring at 2000 rpm for 5 minutes (2 minutes for all the samples except sample T4S1, which was stirred for only 1 minute) then violently beaten with a kitchen electrically driven mechanical whisk to obtain a white foam equivalent to what is known in cooking as whipped egg white. Then the mixture was heated in a microwave for  $T$  minutes. The basic formula has already been presented in reference [26]. Based on this, a series of samples with the heating times of 4 min, 5 min, 6 min and 10 min were named T4, T5, T6 and T10, respectively. Based on the table presented in reference [26], the samples with 25g and 35g of water were named W25 and W35, respectively. Accordingly, F4, F12, F16, CO, C4, C12, and C16 were the samples with different amounts of F and different amounts of camphor. The sample T4S1 was prepared with the stirring time of 1 min. The mixtures used have already been detailed in reference [26]. After drying, either in an oven or by microwave oven [26], the albumin foams were kept in a vacuum oven at 60°C for 15 h, giving bulk density of 0.29g/cm<sup>3</sup>, true density of about 1.25g/cm<sup>3</sup> and porosities of around 77%. The true density was obtained by pycnometer measurement (AccuPyc II 1340, Micromeritics Instrument Corporation). The formulation of the foams subsequently used for silica infiltration was the T4 of composition water 30g, albumin 15g, camphor 4g and formalin 37% solution 8g; microwaved for 4 minutes and with a density 0.190 g/cm<sup>3</sup>.

## 2.2 Preparation of SiC Foams

The foam was infiltrated with tetraethyl orthosilicate (TEOS) by using a proportion of foam to TEOS of 1:8 by weight. The subsequent gel formation was used to fix the silica onto the albumin foam. The TEOS has the remarkable property of easily converting into silicon dioxide. This reaction occurs upon the addition of water:



this hydrolysis reaction being an example of a sol-gel process.

The samples were subsequently calcinated at 500°C. The yield was approximately 5 wt% silica in the form of SiC and the shrinkage amounted to approximately 50%. The corresponding SEM micrographs show the results obtained.

The resulting silica foams obtained from the initial albumin foams were very acceptable, but with a low mechanical stability due to their high porosity.

The samples were not pyrolysed, because it was feared that the protein would not yield any carbon necessary for liquid silicon infiltration.

## Scanning electron microscopy (SEM)

The ceramic foam samples were attached on Al-sample holders with double-side adhesive carbon tabs (Plano, Wetzlar, Germany) and sputtered with gold. The SEM micrographs were obtained with a Quanta 200 SEM (FEI, Brno, Czech Republic) operated at 20 kV.

## X-Ray diffraction (XRD)

Crystalline phase compositions were measured by X-ray diffraction method (XRD). The powder patterns were recorded between 5° and 70° using a Kristalloflex D500 (Siemens, Karlsruhe, Germany), operated with monochromated Cu-K $\alpha$  radiation ( $\lambda = 0.14505$  nm, 30 kV, 30 mA).

## Raman spectroscopy

The ceramic foams were analysed by confocal Raman microscopy (Almega XR, Thermo Fisher, Dreieich, Germany) using a 532 nm laser. The spectra were collected between 250 and 1850 cm<sup>-1</sup>.

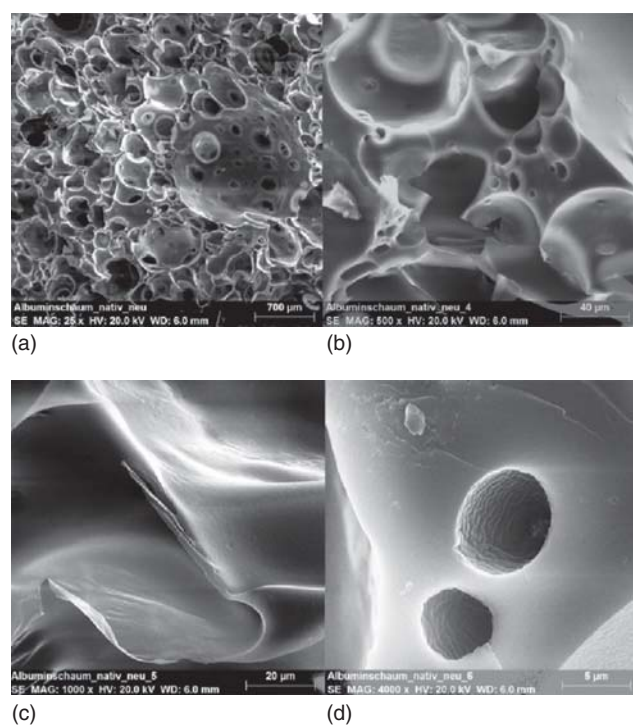
## RESULTS AND DISCUSSION

The Scanning electron microscope images in Figures 1–3 show the transformation of a dry albumin foam [26] into a SiC carbide foam through the different stages of reaction. Thus, in Figure 1 the smooth cell walls of the carbon-based natural albumin foam can be observed at different levels of magnification. Figure 2a–c shows the state of the albumin foam at different magnifications when impregnated with tetraethyl orthosilicate (TEOS). The gel formed by TEOS fixing the silica produced by the sol-gel reaction  $\text{Si}(\text{OC}_2\text{H}_5)_4 + 2 \text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4 \text{C}_2\text{H}_5\text{OH}$  onto the albumin is particularly evident in Figure 2c, where plaques of silica gel are clearly superimposed onto the carbon skeleton of the albumin foam.

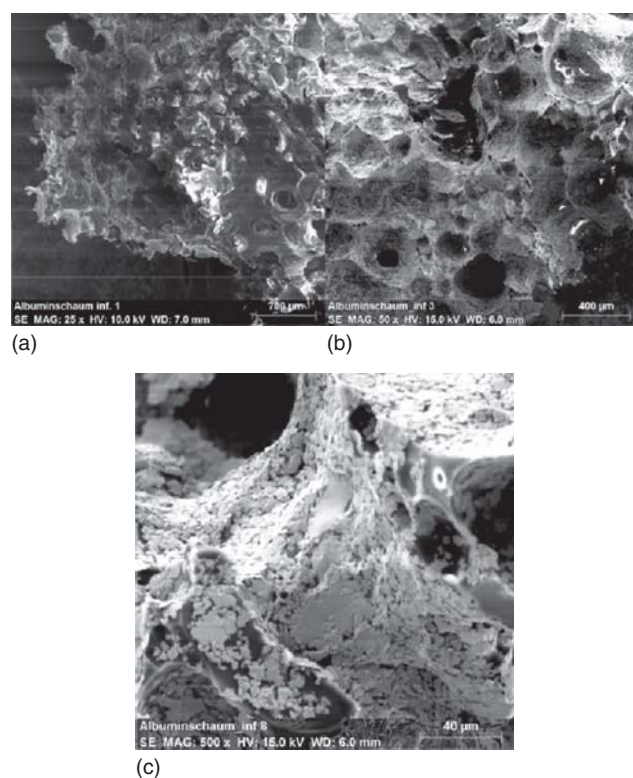
After destruction of the protein by calcination the appearance of the foam rich in SiC is shown in Figure 3a–d. These figures clearly show the totally different appearance of the foam in relation to what is observed in Figure 1. The cells are more jagged and thinner based on the reaction leading to the formation of SiC.

The structure as depicted by SEM is interesting, as the cell windows appear largely open because of the many small holes.

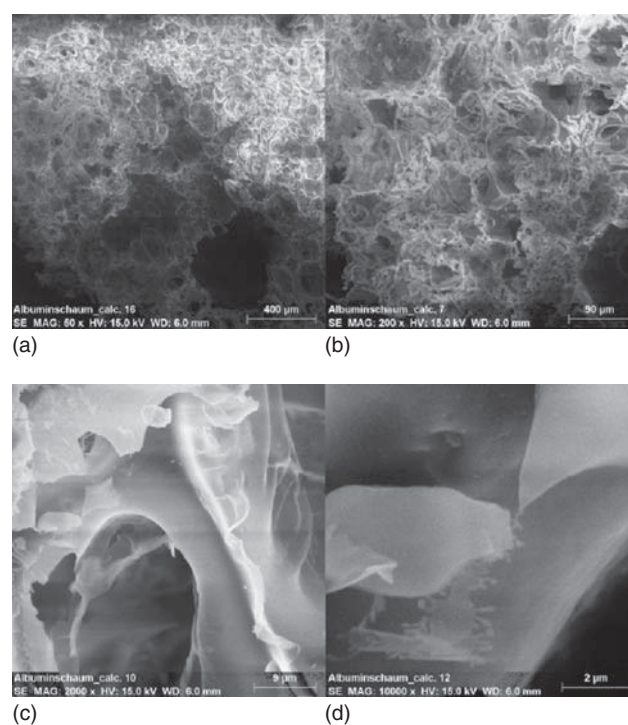
The XRD (Fig. 4) shows very nicely the formation of the polycrystalline SiC after infiltration, which primarily consists of 3C-SiC with some 6H-SiC (pre-peak). Amorphous or crystallised carbon phase were not detected.



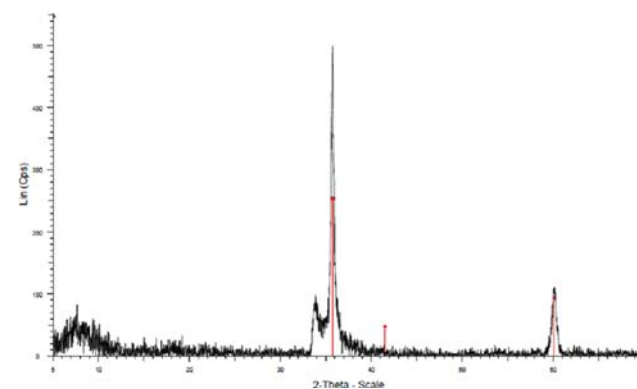
**Figure 1** Original albumin foam at magnification: (a) 25x, (b) 500x, (c) 1000x and (d) 4000x.



**Figure 2** Albumin foam TEOS infiltrated at magnification: (a) 25x, (b) 50x and (c) 500x.



**Figure 3** SiC albumin foam after calcination at 500°C at magnification: (a) 50x, (b) 200x, (c) 2000x and (d) 10000x.



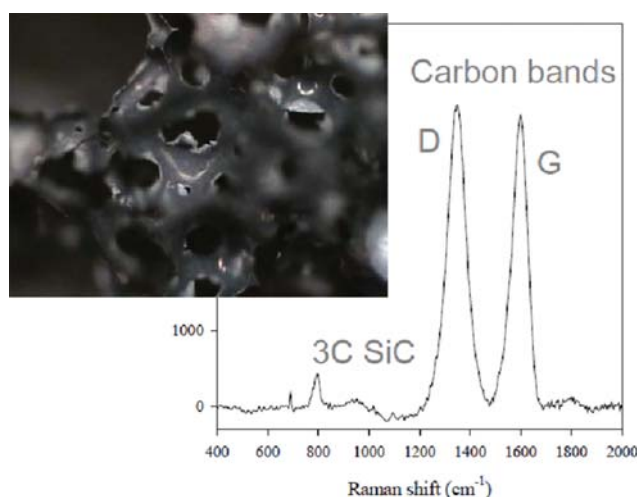
**Figure 4** XRD pattern of the SiC protein foams.

Raman (Fig. 5) shows a rather small 3C-SiC and the prominent carbon related bands (D- and G-band)

It can be concluded that as shown by the SEM, the SiC foam appears very fine grained. This already pointed to the fact that the reaction of the carbon with Si might not be fully complete.

Interestingly, no carbon phases were detected in the XRD. Contrary to this, the Raman spectra distinctly verifies the presence of the disordered carbon phase, which might be X-ray amorphous.





**Figure 5** Raman spectrum of the SiC foam tested.

This means that the foams still contain a considerable amount of carbon in the SiC foams. Optimisation of the parameters for the SiC formation thus appears to be still necessary.

## CONCLUSION

Infiltration of albumin protein foams with tetraethyl orthosilicate (TEOS) and the subsequent gel formation yielded silicon carbide foams once the gel was calcinated at a reasonably low temperature of 500°C. Higher temperatures could not be used as they caused the collapse of the delicate protein foam. The use of scanning electron microscopy to compare the original albumin foam with the final silicon carbide one showed clear differences in the microscopic appearance of the two. The XRD, and in particular Raman analysis, confirmed that a relatively low amount of carbon was converted in SiC, and that further optimisation is necessary to perfect such a process for protein foams.

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