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# Characterization and functionalization by sol–gel route of SiC foams

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**Abstract**

Ceramic foam materials are commonly used for various applications, including catalyst supports or solar receivers. SiC foams are good candidates for the latter application as solar receivers. Its efficiency is directly related to the geometry, which can be evidenced by X-ray microtomography, and optical properties of the receiver. A promising route to add functionalities with homogenous and adhering oxide coatings onto complex SiC foams in a single step process is proposed. This oxide synthetic process is derived from the Pechini method. Foams are fully impregnated by precursor sols with a controlled viscosity making a thin and totally covering coating.



*Keywords:* SiC foam; Sol–gel processes; Impregnation; Oxide coatings; X-ray microtomography

## 1. Introduction

Ceramic foam materials have a large surface area, open-cell porosity, low density, good mechanical strength and good resistance to high temperatures making such porous media commonly used for various applications, including catalyst supports or solar receivers.[1] Foams structure, microstructure and morphology characterizations enable to understand and predict the heat transfer phenomena and facilitate the numerical simulation of radiative transfer or the numerical generation of foams. Heat transfer properties are not only related to the cell size and porosity, but also to struts geometry and dimension.[2,3] A way to extract statistical information from these foams is to characterize them by X-ray microtomography. This non-destructive technique, based on a 3D reconstruction of the sample, allows a precise and quantitative analysis of the foam parameters, which is not easy in traditional 2D analyzes. Pardo-Alonso et al.[4] use X-ray microtomography to characterize polyurethane foams, extracting quantitative structural information from images of the sample 3D reconstruction. In this work, a more specific quantitative structural analysis of SiC foams is presented, showing the complex morphology of such substrate and its open porosity.

As said before, foams are usually dedicated to catalysis or solar applications. If these foams are coated, other functionalities can be brought. For example, $Cr_2O_3$ is a good candidate since it has already proven its efficiency as an oxidation barrier onto metallic support.[5,6] Indeed, stainless steel oxidation that usually occurs at high temperatures is decreased once coated with $Cr_2O_3$. The coating has to be adherent, continuous and covering in order to insure the complete substrate protection. It also has to support high temperature cyclings without crack formation. A versatile and very promising route to synthesize $Cr_2O_3$ is the sol–gel route, following the Pechini method.[7] A polymerization reaction between organic compounds followed by the chelating of metallic cations enables the formation of oxides. It is thus possible to control the sol viscosity and coating microstructure. Coatings made via liquid route, especially sols, are widely used and often prepared by the dip-coating technique.[8] Our main challenge is to cover the entire foam surface, to keep an open porosity, while preserving the homogeneity and adherence of the coating. This depends on essential parameters such as the sol viscosity and precursors concentrations. Some methods of SiC foam impregnation have already been developed. Vargová et al.[9] realize a $TiO_2$ coating using the dip-coating method but they need to proceed several times in order to obtain the final

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coating. Amrousse et al.[10] realize an alumina layer on SiC foam using a hydrothermal technique, however the coating is non adherent and presents several cracks. In this study, an easy and fast method is proposed to perform homogenous and adherent oxide coatings. The viscosity is easily controlled by acting on the kinetics of the polymerization reaction. Sols are synthesized and then used to coat several substrates in only one step, even if the substrate has a complex morphology and an uneven and rough topography.

## 2. Materials and methods

### 2.1. Commercial ceramic foams

Commercial β-SiC foams (SICAT company, France) with an opened porosity of 15 ppi (pores per inch, which corresponds to a pore diameter of 2.8 mm), and a mean size of 20 mm × 20 mm × 10 mm were used in this study. The specific surface area is about 28 $m^2\ g^{-1}$. They are manufactured by impregnating a polyurethane template with a precursor slurry which leads to SiC foams after a thermal treatment and carbonization of the template.

### 2.2. Preparation of the coating and impregnation of foams

A route derived from the Pechini's patent[7] was used to synthesize a precursor sol which leads to the formation of a metallic oxide ($Cr_2O_3$ in this study) after a suitable heat treatment that we will discuss later. With this low-cost process it is possible to easily coat various substrates controlling the sol viscosity. Coatings obtained after a heat treatment are also homogenous at a molecular scale and the stoichiometry is totally controlled.

Two kinds of starting materials are used: inorganic compounds (metallic nitrates) provide cations and organic compounds (acetylacetone (acac, chelating agent), hexamethylenetetramine (HMTA, polymeric precursor)) form a polymeric chain with a homogenous cation distribution in the structural network. The precursor sol is prepared using acetic acid and water as solvents.

Nitrates $Cr(NO_3)_3$, $9H_2O$ are dissolved in 5 mL of distilled water, three concentrations are used in this work: 0.5 M, 1.0 M, 1.5 M. Organic compounds (HMTA and acac) are dissolved in acetic acid with a molar ratio of 1:1. Nitrates and organic compounds are then mixed with a ratio of 1:3.1 according to previous work[11] giving a solution with a final volume of 25 mL. The kinetics of the polymerization reaction is increased when heating the mixture during 5 min at 60 °C.

SiC foams were totally immersed into the precursor sol during few minutes and the excess of sol was removed by an air jet. According to previous works[12] the samples were calcined in air at 800 °C during 2 h with a heating rate of 100 °C/h. Since organic compounds are being removed up to 400 °C a slow heating rate is necessary to avoid the formation of cracks in the coating. In parallel, a part of the sol was calcined in the same conditions in order to more easily characterize the crystalline phase.

### 2.3. Characterization techniques

Structure, microstructure and morphology of foams were characterized. Structure was determined by X-ray diffraction using a BRUKER AXS D4 Endeavor diffractometer operating with a Cu-Kα radiation source after sample grinding.

Microstructural information of the SiC foam was obtained by scanning electron microscopy (JEOL JSM–6510LV).

Morphology of the SiC foam was firstly determined with a 3D optical microscope KEYENCE (magnification 20–200×). To obtain statistical information, X-ray computed microtomography images were obtained with a Phoenix/GE Nanotom 180 instrument using a tungsten target. The acquisition parameters were a voltage of 90 kV and a current of 100 μA, a binning of 1 × 1 and a time of 1000 ms. Data were processed with Datosx reconstruction software in order to obtain 3D images of SiC foams.

Sols and coatings main features were also characterized. The sol viscosity was measured at 21 °C with a shearing viscometer Lamy Rheomat RM 100. Contact angle was measured with a DIGIDROP Fast 60-GBX device. A SiC pellet was used with the same chemical composition as the SiC foam to facilitate the measurement of the angle. Even if the porosity or roughness are different from the pellet to the foam, this method seems to be the more suitable to evaluate the wettability range.

Powders obtained after sol calcination were then characterized by X-ray diffraction. The coating microstructure was determined with a scanning electron microscope JEOL 8700F. Thermogravimetric and differential thermal analyzes were carried out to determine thermal behavior of foam with and without coatings with a Setaram TGA-DTA 92 instrument up to 1200 °C at 1 °C/min under air.

## 3. Results and discussion

### 3.1. Characterizations of uncoated SiC foams

#### 3.1.1. Chemical composition

Firstly, chemical composition of the SiC foam samples was controlled by Inductively Coupled Plasma (ICP) and an excess of 9% of carbon was measured. Moreover, some impurities were detected such as Fe, Al, Ca or Mn in very low concentrations (less than 500 ppm) compared to Si and C concentrations. The pyrolysis of the polyurethane template during the manufacturing process involves this carbon excess while the impurities are probably due to the binder used during the process.

#### 3.1.2. Structural and microstructural characterizations

X-ray diffraction patterns were performed on ground SiC foams at room temperature (Fig. 1). Silicon carbide can be found in various polytypes particularly in cubic and hexagonal structures. The SiC was crystallized and the XRD pattern was indexed in the cubic structure with a F-43 m space group and noted 3 C in the Ramsdell notation (JCPDS n°00-029-1129). The shoulder observed at $2\theta = 33°$ corresponds to a stacking fault in the structure.[15]