Journal of Alloys and Compounds 694 (2017) 921–928

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Electrically conductive gamma-alumina/amorphous carbon nano-composite foams

Chiara Dionigi [a, *], Tanja Ivanovska [a], Luca Ortolani [b, **], Vittorio Morandi [b], Giampiero Ruani [a]

[a] Consiglio Nazionale delle Ricerche, Istituto per lo Studio dei Materiali Nanostrutturati, Via P. Gobetti 101, I-40129 Bologna, Italy
[b] Consiglio Nazionale delle Ricerche, Istituto per la Microelettronica e Microsistemi, Via P. Gobetti 101, I-40129 Bologna, Italy

ARTICLE INFO

Article history:
Received 26 July 2016
Received in revised form
5 October 2016
Accepted 6 October 2016
Available online 7 October 2016

Keywords:
Capsules
Alumina
Templating method
Electrical properties
TEM characterization

ABSTRACT

The templating method has always been considered an efficient method to design new morphologies for old materials. We have already demonstrated that it is possible to generate by templating method, a new class of alumina meso-foams showing peculiar conductive properties that strictly depend on the size of the bubbles generated by polymeric templating beads.

In this work we definitively demonstrate by the "high resolution transmission electron microscopy" and by the "Energy Dispersive X-ray Spectrometry (EDS)" that the alumina meso-foams are actually composites of conductive amorphous carbon and γ-alumina nanoparticles. This evidence supports the hypothesis that the conductive properties of the meso-foams are mainly due to the un-combusted amorphous carbon imbedded in the alumina frame.

We believe that our innovative approach based on in-situ carbon-composite formation, could be potentially extended to several other non-conductive oxides shaped through the old templating method.

1. Introduction

Submicrometric foams of metal oxide materials have attracted great attention in the field of the engineered ceramics [1]. Inorganic foams are undoubtedly low-density materials where the inorganic material, which represents the frame of the scaffold, expresses the chemical and physical properties of the foams. It is worthy to note that the foams have found applications in optics [2], photonics [3], sensors and magnetism [4,5]. Moreover, the possibility of changing the conductive characteristics of the bulk metal oxide only by controlling the morphology of the inorganic scaffolds at a sub-micrometric scale seems to be particularly appealing for all proposed applications.

A sustainable method for the generation of meso-foams of γ-alumina made of aggregates of monodispersed alumina capsules, fabricated from aqueous solution and in ambient conditions, has recently been presented [6]. The mechanism for capsules formation has already been demonstrated in ref. [6] through the interactions of aluminium-sec-butoxide in water, i.e. the aluminium oxide precursor used for the fabrication, with the surface of the polystyrene beads that are used as templates. The meso-foams are formed after template removal by calcination.

Indeed, the observed conductivity might be a direct result of the combustion process of the templating agent, resulting in conductive carbonaceous residues within the meso-foam, similarly to the reported findings in refs. [7–9] for the fabrication of semi-conductive ceramics by combination of gel-casting and reduction sintering.

It is noteworthy that the surface carbon-coating technique [10,11] is a well-known method used to improve the surface electronic conductivity and the electric quality of the contact between inorganic particles, and to significantly improve the electrochemical performance of different inorganic materials.

We demonstrate here, for the first time, that the alumina nanoparticles forming the meso-foams are embedded into a matrix made of amorphous carbon generated after calcination in air at temperature below 800 °C in the conditions reported in ref. [6], and that the conductive characteristics of the meso-foams depend on the composition of such amorphous matrix.

To support this hypothesis, already proposed in the previous

* Corresponding author.
** Corresponding author.
E-mail addresses: c.dionigi@bo.ismn.cnr.it (C. Dionigi), ortolani@bo.imm.cnr.it (L. Ortolani).

http://dx.doi.org/10.1016/j.jallcom.2016.10.056
0925-8388/

article [6], we presented here an estimation from TGA results of the carbon contents with respect to the size of the polymeric beads used in the meso-foam fabrication.

We believe that our approach based on the formation of a nanostructured carbon-alumina composite could be extended to several other non-conductive oxides, with great potential for photovoltaic [12] and energy storage [13] applications.

We explored by transmission electron microscopy (TEM) the presence and the distribution of carbon residuals generated in situ during the calcinations at 400, 600 and 800 °C. We show that the residuals generated at 400 °C and the alumina particles are co-dispersed, homogenously, throughout the meso-foams and that their distribution and presence is modified above 600 °C. The influence of the dispersed carbon on the thermal stability of the meso-foams is also investigated.

2. Materials and methods

2.1. Aqueous suspension of polystyrene beads and aluminium-sec-butoxide

Aluminium-sec-butoxide ($Al(OBu)_3$) was used as the alumina precursor and a solution of $Al(OBu)_3$ [97%, Sigma-Aldrich] in 99% isopropyl alcohol (i-PrOH) was prepared at room temperature following the procedure reported in Ref. [8]. Alumina capsules were obtained after calcination of a dry aqueous suspension containing polystyrene beads (PSB) [14] and $Al(OBu)_3$ [6]. The suspension was obtained mixing in milli-Q water PSB suspensions and aliquots of the $Al(OBu)_3$ solution in isopropanol and leaving the reagents at 50 °C for 24 h. The experimental details, for samples A, B and C, are reported in Table 1, where PSB concentration refers to the bead concentrations in the final PSB/$Al(OBu)_3$ suspensions used in the meso-foam fabrication.

The PSB concentration was calculated by gravimetric analysis of the dry PSB suspension considering that the density of polystyrene is 1.04 g/cm^3 and the volume of a PSB is easily calculated from the PSB diameter.

2.2. Alumina meso-foams from PSB/$Al(OBu)_3$

Suspensions of samples A, B and C were left into glass beakers inside a drying oven at 50 °C until the liquid phase was completely evaporated. Afterwards they were thermally processed in air using a tubular furnace up to temperatures of 400, 600 and 800 °C with a thermal ramp of 1 °C/min followed by a 2 h dwell time at these temperatures. The samples were named "X-T", where X defines the templating PSB: i.e. A, B, C, and T is the calcination temperature: i.e. 400, 600, 800 °C.

2.3. Characterization methods

2.3.1. Thermogravimetric (TGA) and differential scanning calorimetric (DSC) analysis on dried aqueous suspension of PSB/$Al(OBu)_3$

Suspensions of PSB/$Al(OBu)_3$ were gently dried at 50 °C and analysed in air with a STA1500 system, a thermogravimetric analyser equipped with a simultaneous thermal analyser, ramping up the temperature to 900 °C (temperature ramp of 2 °C/min).

2.3.2. Electrical investigation

150 μL of each aqueous suspension of PSB/$Al(OBu)_3$ was deposited (in three consecutive depositions of 50 μL, dried at 50 °C) on glass substrates, and calcinated at 600 °C to obtain 1 cm wide meso-foam films i.e. samples A, B and C (for further experimental details review Section 2.2. 100 nm top Ag contacts were deposited on the films via evaporation using a transistor patterned mask with 70 μm channel length. Electrical measurements were performed at room temperature and ambient light by recording current-voltage characteristics using a Keithley 2400 SourceMeter.

2.3.3. Transmission electron microscopy characterization and sample preparation

TEM characterization has been performed using a Tecnai F20 microscope operated at 200 kV, equipped with EDAX energy dispersive X-ray spectrometer (EDS) for elemental analysis. The 9 films of A, B and C meso-foams calcinated at 400, 600 and 800 °C, were scratched from the silicon substrate, collected and dispersed in isopropanol using sonication for 10 min. The prepared solutions were drop-casted onto conventional TEM copper grids, covered with holey amorphous carbon film.

2.3.4. Scanning electron microscopy (SEM) characterization

SEM observations on samples were performed using a Zeiss FEG-SEM LEO 1530 electron microscope at 5 kV and equipped with an Oxford INCA energy dispersive X-ray spectrometer for elemental analysis.

3. Results and discussion

It was already demonstrated (ref. [6]) that calcination of dried aqueous suspension of PSB in $Al(OBu)_3$ solution at 400 °C results in the formation of monodisperse alumina capsules (Fig. 1).

3.1. Temperature effect on capsules formation

TGA and DSC analyses were both performed on the samples A, B, C (Fig. 2) applying a thermal ramp comparable to the ramp used in the calcinations. From the DSC curve both endothermic and exothermic processes below 600 °C are evidenced [15]. The endothermic processes are due to water and to polystyrene evaporation, where the exothermic processes are due to the combustion of organic molecules and compounds. The abrupt decrease in weight (TGA curve) just below 400 °C indicates that this is the minimum temperature for the removal of the organic component of the sample.

It was evident from the SEM studies on capsules formation [6] that the increment of the temperature affected the capsule morphology and stability. Indeed, the capsules started to brake at 600 °C, after a dwell time of 2 h. At 800 °C the temperature effect is dramatic; from the initial SEM analysis reported in ref. [6], only the trace of the smallest capsules (sample A) seemed to remain on the silicon substrate, and the shells of the largest capsules (sample C) seemed to turn into a porous net of alumina particles.

Table 1
Sample preparation details.

Sample	PSB diameter[a] (nm)	PSB conc. (g/L)	PSB conc. (mol/L)	PSB surface (nm^2/mL)	$Al(OBu)_3$ conc. (mol/L)
A	135	0,9	$7{,}3\cdot10^{-4}$	$4.285\cdot10^{18}$	$6{,}60\cdot10^{-3}$
B	235	0,12	$8{,}7\cdot10^{-6}$	$3.469\cdot10^{17}$	$0{,}60\cdot10^{-3}$
C	395	0,25	$2{,}2\cdot10^{-5}$	$4.185\cdot10^{17}$	$0{,}70\cdot10^{-3}$

[a] Measured by SEM on dried samples.