

Preparation of carbon coated ceramic foams by pyrolysis of polyurethane

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Abstract Electronically conducting carbon coatings over alumina foams were prepared by the foams' impregnation in a polyurethane solution, followed by pyrolysis of the polymer layer. An optimal coating procedure was developed, using a commercial polyurethane lacquer. Pyrolysis was performed by heating the coated foams to 650–1,200 °C in Argon for 2–8 h. Coating characterization included surface area, phase composition, morphological and electrical conductivity measurements. Auger electron spectroscopy (AES) showed the composition was mostly carbon, with trace levels of oxygen impurities. Thickness, microstructure and interface between the alumina foam surface and the carbon film were analyzed using scanning electron microscopy (SEM and HR-SEM). The carbon film's specific electrical resistivity was 1–10 ($\Omega \text{ m} \times 10^{-2}$), depending on the pyrolysis time, temperature and number of coatings. The resistivity was found to decrease by a factor of six when the pyrolysis temperature was increased from 750 to 1,200 °C. A second carbon layer, reduced the resistivity further by about a factor of two. These effects are attributed to densification, improved connectivity between the carbon grains and an overall thickening of the carbon layer. Thermal analysis and Raman measurements on the carbon films point to a grain rearrangement that is consistent with the improved conductivity of the films.

Introduction

Ceramic foams are being used in increasing number of industrial applications such as filtration, thermal insulation and catalytic supports. This growing usage stems from the foam's favorable properties such as low density, mechanical strength, high permeability, thermal and chemical stability. The combination of properties above, make ceramic foams an excellent candidate for electrode applications, especially at high temperatures. The majority of ceramic foams are based on cordierite and various alumino-silicates. These materials are stable at high temperatures and in aggressive chemical environments, however, they are electrically insulating. Therefore utilization of ordinary ceramic foams as electrodes has not been possible.

The main thrust of this work has been to coat ceramic foams with a conductive layer, which is stable at high temperatures and aggressive process conditions. The intent is to use these carbon coated foams both as stand-alone products and as an under layer in electrolytic or other deposition processes for electrode or catalyst supports applications.

Many methods to form carbon-coated ceramics are practiced. For example, spin coating photoresist layer on a silicon wafer followed by its pyrolyzation [1]. Another recent approach to coat alumina with carbon is based on adsorption of acetyl acetone on the alumina support followed by its subsequent thermal treatment under a vacuum [2]. Konno et al. obtained carbon coated ceramic particles (TiO_2 , Al_2O_3 , MgO) by mechanical mixing of these particles with 20–50% polyvinylchloride (PVC) powders. The mixture was then heated to 1,000 °C at a rate of 500 °C/h in an inert atmosphere and soaked at 1,000 °C for 1 h to carbonize

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the PVC [3, 4]. Another example of carbon coating is the carbon film electrode (CFE), which in most cases is prepared by chemical vapor deposition (CVD) technique. In this process a low molar mass gaseous hydrocarbon, usually methane, is mixed with an inert carrier gas and introduced into a heated reactor. Chemical reactions generating solid carbon occur on the heated substrate surface or in its vicinity. The carbon is deposited as a thin film, and thus the electrodes obtained are referred to as pyrolytic carbon film electrodes (PCFEs). The main advantage of the PCFE is the large decrease in the residual current, which has been shown to be particularly important in analytical procedures utilizing pulse voltametric techniques [5].

Mechanical mixing of foams and carbon is not feasible since the coating will take place preferentially on the outer surface, leaving the internal surface uncoated. In addition the foam is not sufficiently strong to bear the mechanical forces during mixing. To overcome these obstacles, an impregnation method was carried out. Polyurethane (PU) was selected as a raw material since it is readily available, has a good adhesion to alumina and was found to leave a significant carbonaceous layer (4–5% wt.) during pyrolysis. In contrast to PU, other polymers that were tested included polystyrene, polyethylene, polypropylene, polymethylmethacrylate (PMMA) were found to adhere badly to the Al_2O_3 surface and their carbon residue was insufficient and non-uniform. During impregnation the foam is first soaked in a polymer solution of polyurethane, then dried to form the polymer coating. The coated foam is then heated under inert conditions to induce polymer pyrolysis and form the conductive carbon layer. Impregnation is suitable here because it enables the solution to penetrate into the cellular structure, and coat the entire foam surface with the polymer film.

Experimental

Preparation of the ceramic foam

Infiltrated ceramic foams were made by the polymeric-sponge method [6]. The method is based on infiltration of a polymeric sponge with a ceramic slurry. The initial polymeric sponge (BULPREN S 28133, RECTICEL, density: 30 kg/m^3) was cut into rectangular shapes. Typically, the sponge is compressed to remove air, immersed in the slurry, then allowed to expand. After the excess slurry is drained, the infiltrated foam is dried to deposit the ceramic particles on the sponge. The dry reticulated structure is heated in air to $800 \text{ }^\circ\text{C}$ to drive off the organics from the slurry and to burn out the

polymeric sponge. During the burnout stage (below $1,000 \text{ }^\circ\text{C}$), a considerable amount of gaseous products are evolved. Therefore, slow heating is critical in this stage to keep the ceramic structure intact. The final step is densification of the ceramic matrix by sintering at higher temperatures. The sintering temperature depends on the ceramic material selected for the foam. In the present case the alumina (Al_2O_3) is sintered at $1,650 \text{ }^\circ\text{C}$ for 9 h in air [6–8]. During the firing step, the foams' rectangular shape was retained, however shrinkage of about 20% occurred. The final dimension of the samples was approximately $15 \times 10 \times 5 \text{ mm}^3$.

Coating the ceramic foams

Impregnation was carried out by immersion of the Al_2O_3 foams into a dilute solution of commercial polyurethane lacquer (Tambur, Dor 120, transparent polyurethane). This product is a mixture of two segments: a lacquer and a solvent. Four concentrations of the lacquer in the mixture were examined: 60, 70, 80 and 90%, (volume percentage). After the immersion and drying at room temperature for 24 h, the impregnated foams were heated, ($300 \text{ }^\circ\text{C/h}$) in argon at $750 \text{ }^\circ\text{C}$ for 2 h. Based on these tests, additional samples were prepared at a concentration of 70%, and pyrolysed at several temperatures: 650, 750, 850, 1,000 and $1,200 \text{ }^\circ\text{C}$ for 2 h. The aim was to investigate the influence of carbonization temperature on the electrical conductivity. To check the effect of carbon loading on the conductivity, a second layer of polymer was applied over the carbonized layer, followed by the same pyrolysis conditions. The average carbon loading in the single and double coated foams were 4 and 6% wt., respectively. The pyrolysis soaking time was changed from 2 to 8 h, to find out the influence of the sintering time on the electrical conductivity and structure.

Sample characterization

After carbon coating, the ceramic foams were observed under optical microscope, scanning electron microscopy SEM (JEOL JSC 5400, Japan) and HR-SEM. The carbon loading was measured directly by weighting the foam before and after impregnation and carbonization. The crystal structure of alumina was identified by X-ray powder diffraction (XRD) using a D5000 powder diffractometer (Siemens, Germany) employing Cu-K_α radiation. Since the material was fired at $1,650 \text{ }^\circ\text{C}$, the $\alpha\text{-Al}_2\text{O}_3$ phase is present. Thermal analysis (TGA/DTA) was conducted in a Setaram TG-92 unit under flowing argon ($1.8 \times 10^{-3} \text{ m}^3/\text{h}$) with a heating rate of $300 \text{ }^\circ\text{C/h}$ and sample mass of 40–50 mg. The phase and

structure of the carbon layers were characterized by μ -Raman spectroscopy using a 514.5 nm excitation of Ar^+ laser and a PC-interfaced “Dilor” micro-probe facility in air under ambient conditions. The scope uses a 1,000 \times objective lens to focus the laser beam onto a 1 μm spot on the carbon surface. A set of two scans (10 min each), were captured at a 3 mW laser power for each sample. Microlab 350—Auger electron spectroscopy (AES) (Thermo VG Scientific) was used to determine the chemical composition of the films. Specific surface area (SA) of carbonized foams was determined by a single point BET method (nitrogen adsorption–desorption at 77 K) using a Monosorb Quantachrom instrument.

A standard four-probe method was used to measure the resistivity of the carbon coated foams. The electrical resistivity, r , is given by [9]:

$$r = \frac{(V/I)}{L} \cdot S_{\text{eff}} \quad (\Omega \cdot \text{m}) \quad (1)$$

where L (m) is the distance between the inner two voltage (V) contact points, I is the current connected to the outer two contact points. The solid cross section area of the solid, S_{eff} (m^2), is equal to the overall area times the relative density. In this work, the relative density is $\sim 20\%$ of the theoretical value of fully dense Al_2O_3 . The electrical conductivity σ is the reciprocal of the measured resistivity.

Results and discussion

Effect of lacquer concentrations

A representative optical micrograph of a pure alumina foam and a carbon coated foam is shown in Fig. 1. From this micrograph, it was found that there were no differences in the overall dimensions of the foams before and after carbonization, except for the expected color change.

Four concentrations of lacquer (part A) were examined: 60, 70, 80 and 90% (volume percentage). The electrical resistivity of the foams was checked after pyrolysis of a single coating. The same foams were coated and pyrolyzed again, and their resistivity was re-measured. As shown in Fig. 2, the resistivity of the double-coated samples is lower than the singly coated samples over the whole concentrations range. This can be explained by: (a) extra densification of the first layer being carbonized twice, (b) insertion of additional carbon into the voids and grain boundary gaps in the first layer, and (c) thickening of the carbon layer.

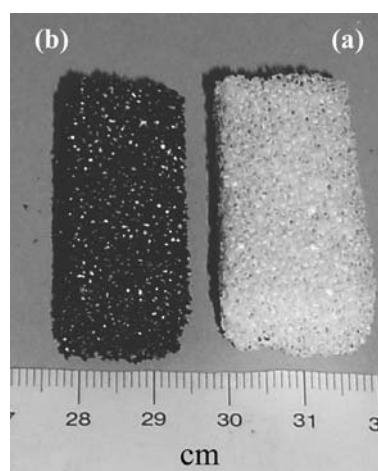


Fig. 1 Optical micrograph of alumina foam, (a) before and (b) after carbonizing

A minimal resistivity was found for the 70% mixture. A possible explanation of this minimum is poor adhesion of the more concentrated solutions due to higher viscosity that cause inhomogeneous coating of the polymer. On the other hand, at lower concentrations the carbon layer continuity is possibly damaged.

Thermal analysis of polyurethane pyrolysis

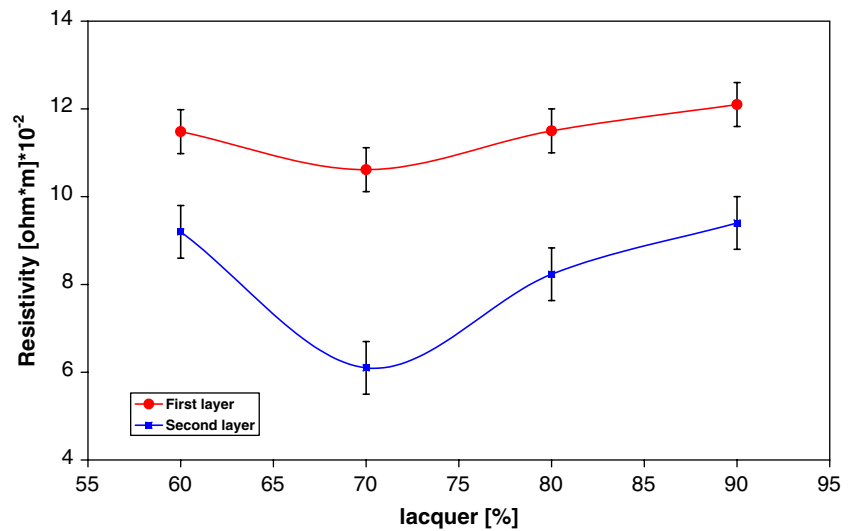
TGA/DTA measurements were made to study the polyurethane film pyrolysis and to define the carbonization stages. A typical TGA/DTA pattern of alumina foam impregnated with polymeric lacquer is shown in Fig. 3. The pattern is divided into the following three steps: (a) In the 20–230 $^{\circ}\text{C}$ range, the weight is nearly constant, however three endothermic peaks are seen. This step apparently involves an internal chemical decomposition of the polymer without evolution of volatile compounds.

(b) In the 230–470 $^{\circ}\text{C}$ range, a significant weight loss of 4.2% was measured. This weight loss is related to evolution of gaseous products during the second step of polyurethane thermal degradation.

(c) In the 500–950 $^{\circ}\text{C}$ range, the heat flow curve shows a wide exothermic peak. This exothermic effect is not accompanied with any weight loss and could be attributed to carbon grains rearrangement to a film with a lower energy state and possibly lower surface area. It is possible that this effect is due to Ostwald ripening effect.

According to these findings, the carbonizing temperatures were set for next experiments, and the morphology and electrical conductivity were investigated after every isothermal annealing at selected temperatures. Based on the original weight of

Fig. 2 Resistivity vs. lacquer concentrations for samples which were carbonized at 750 °C, first and second layers



the alumina foam the % conversion of PU to carbon is calculated to be 4–5% wt.

Effect of carbonizing temperature

The samples with 70% lacquer concentration (optimal concentration) were pyrolyzed at temperatures chosen based on thermal analysis data: 650, 750, 850, 1,000 and 1,200 °C for 2 h. The aim was to investigate the influence of carbonization temperature on the film morphology and electrical conductivity. After measurements a second carbon coating was applied to the foams followed by identical pyrolysis conditions as the first coating.

Coating morphology

The structure of the carbon coating on the alumina backbone is shown in the SEM and HR-SEM micrographs in Fig. 4(a, b) present a carbon coated foam, while (c, d) present a pure alumina foam surface. As seen in Fig. 4(c, d) the Al_2O_3 grain boundaries are clearly noticed, while in (a, b) the boundaries between the grains are smoothed by the carbon coating. The carbon coating is continuous and follows the contour of the alumina grains.

The cross section of the foam’s struts is triangular, as seen in Fig. 5a. The hollow central section of the Al_2O_3 strut was the location of the starting polymeric sponge,

Fig. 3 A typical TGA/DTA pattern for alumina foam impregnated in polymeric lacquer, heated in Argon atmosphere

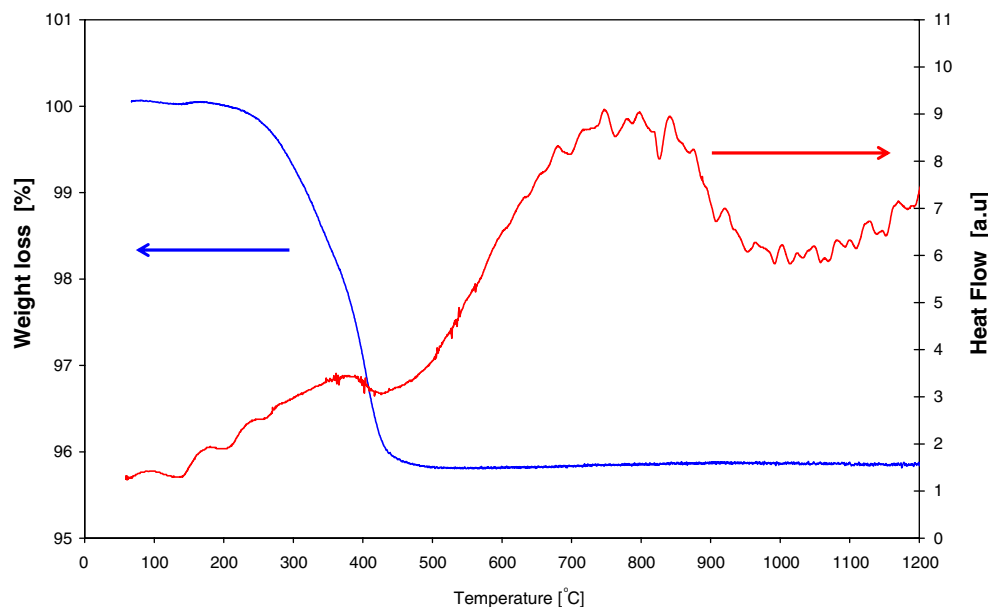
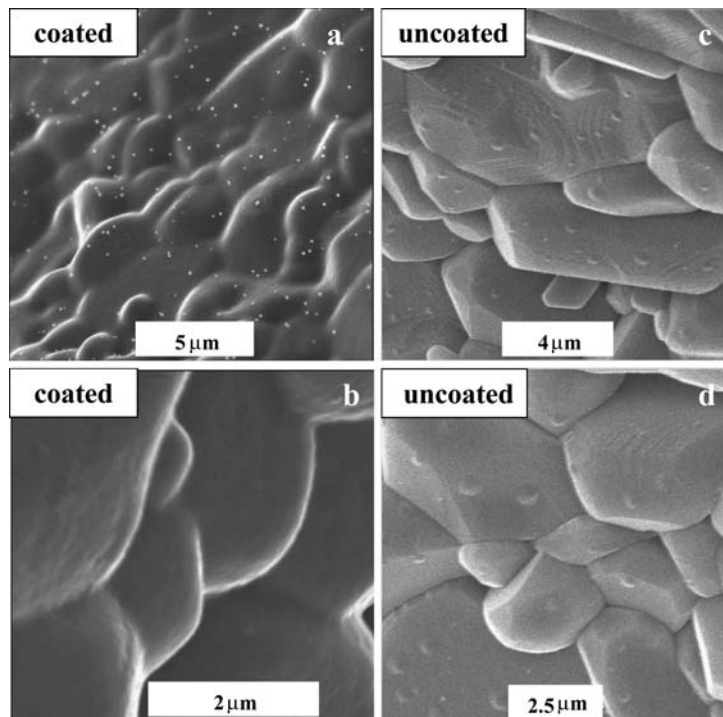


Fig. 4 SEM and HR-SEM micrographs of alumina foam surface area with carbon coating (**a, b**) and without coating (**c, d**)



which was burned out. In Fig. 5a the carbon layer can barely be noticed. Figure 5b is a magnification of one corner of the strut in Fig. 5a. The broken surface exposes the underlying Al_2O_3 grains and the uniform nature of the carbon coating. Figure 5c is a further magnification of the marked square in Fig. 5b. The boundary between the broken carbon layer and the alumina grains is definitely seen. The observed small debris particles over the surface formed as a result of the breaking of the coating. The thickness of the carbon layer in this image is 870 nm, the thickness range that was calculated from more than 100 images, is 500–1,200 nm. Figure 6 presents a view of the width of the carbon layer. The interface between the alumina grains and the carbon layer is shown in Fig. 6b. The lack of gaps and intimate contact of the carbon layer and the alumina under layer is a prerequisite for adhesion of the carbon layer to the foam surface. The carbon grains can be vaguely noticed here, some of them are marked by circles in Fig. 6b, their size is in the order of a few tens of nanometers.

The structure evolution of the carbon coating as a function of carbonizing temperature is shown in the SEM micrographs in Fig. 7: a. 650 °C; b. 850 °C; c. 1,200 °C. At low temperature (650 °C), large islands/aggregates are observed among the smaller grains. At a carbonizing temperature of 850 °C, the carbon grains are more pronounced, and large aggregates are not observed. At the highest temperature (1,200 °C), the carbon grains look like they are better packed. Almost

no porosity is seen and the surface is smoother and more homogeneous. The effect is totally due to rearrangements within the carbon layer, since the alumina had been pre-fired at 1,650 °C thus no changes are expected in the alumina microstructure at relatively low temperatures of 1,200 °C.

Electrical conductivity measurements

The electrical measurements are consistent with the morphological observations described above. The voltage decreases to half its value while the carbonizing temperature rises from 750 to 850 °C, as seen in the insert of Fig. 8, the constant slope allows the resistivity to be calculated. As the carbonization temperature rises to 1,200 °C, the electrical resistance decreases further. Clearly the second layer lowers the resistivity of the carbon coating over the whole temperature range. The relative improvement in the resistivity due to the second carbon layers is roughly 50% (40% at 750 °C to 60% at 1,200 °C). Since the coating procedures were identical, this result is consistent with doubling the effective thickness of the carbon layer. It should be noted, however that the second layer has two effects: (a) filling the cracks or gaps (along carbon grain boundaries) in the first layer, and (b) increasing the overall thickness of the carbon layer. Both effects increase the effective cross sectional area of current transport, thus reducing the resistivity. Experiments were carried out at lower temperature of 650 °C, but

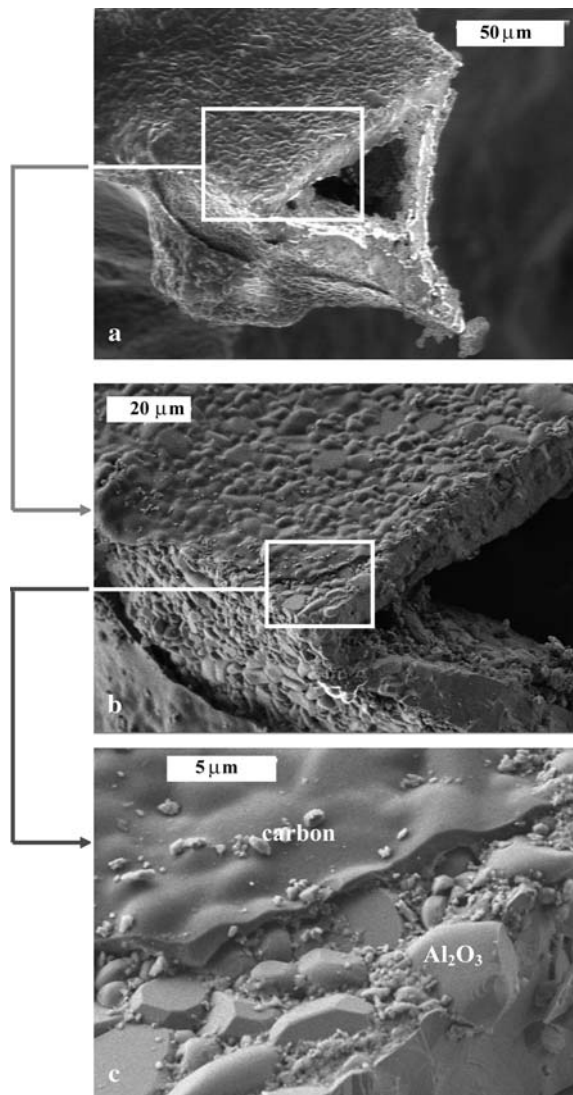
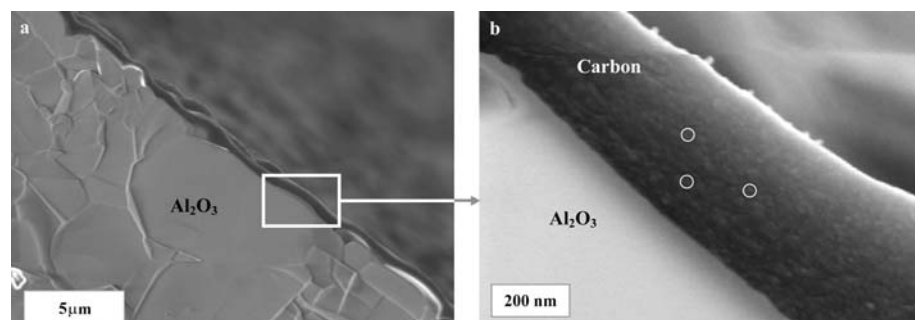


Fig. 5 HR-SEM micrographs of a cut profile strut and a broken carbon coating

the values of the resistivity were in the mega-ohm range and thus are not presented. This high resistivity suggests that the connectivity between the carbon grains is below the percolation limit during pyrolysis at 650 °C. Removal of the surface oxygen groups by

Fig. 6 HR-SEM micrographs of (a) cut profile strut and (b) a magnification of the interface between the alumina and carbon layer



calcination in an inert atmosphere leads to a significant reduction in electrical resistivity [10].

Surface area (SA) measurements by gas adsorption-desorption (BET method), were conducted in order to examine the carbonizing temperature influence on the specific surface area. The initial SA of the alumina foam before coating was nearly zero. It should be noted that porosity in our foam is on the macro scale, with pores in the millimeter size range (see Fig. 1). The density of the foam is about 800 kg/m³, which for an Al₂O₃ (full density of 4,000 kg/m³) means that we have about 80% porosity. This macro-porosity, however does not lead to any appreciable surface area because this alumina backbone is fired at 1,650 °C, where the grains grow appreciably and the meso- and micropores disappear as the material densifies. The meso- and micropores range from 0.5 to 100 nm can give rise to significant SA, however because these pores disappear during firing, the final SA is expected to be small. In the present case the average grain diameter is on the order of five micron (see Fig. 4). The calculated specific surface area of the material is ~0.25 m²/g. This area is very tiny and is close to the detection limit of our BET measurement system. This result was not changed after the coating and carbonizing procedures. Suggested explanation is the almost negligible weight fraction of the carbon relative to the whole foam specimen. Changes at the thin carbon film cannot be detected by SA measurements.

XRD pattern of carbonized alumina foam did not show the formation of Al₄C₃, suggesting no reaction between carbon and alumina at 1,200 °C. If Al₄C₃ had formed at the interface of the carbon film and the alumina, it would have been detected [4].

Chemical composition of the film

Auger electron spectroscopy (AES) was used to determine the impurity levels in the film. High impurity concentrations could create significant defects in the carbon crystalline lattice, leading to deterioration in the electrical conductivity. Figure 9 shows a differentiated

Fig. 7 SEM micrographs of the carbon coating layer at different carbonization temperatures: (a) 650 °C; (b) 850 °C; (c) 1,200 °C

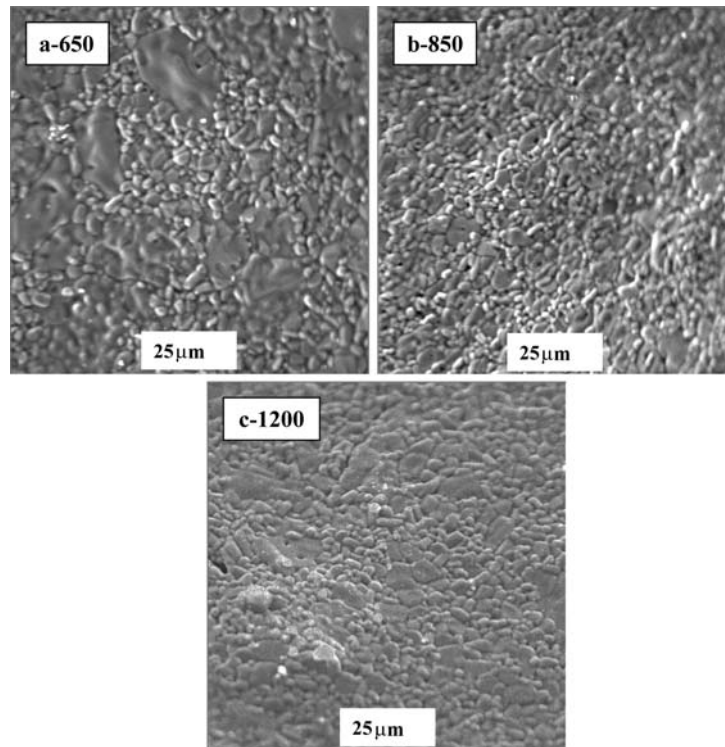
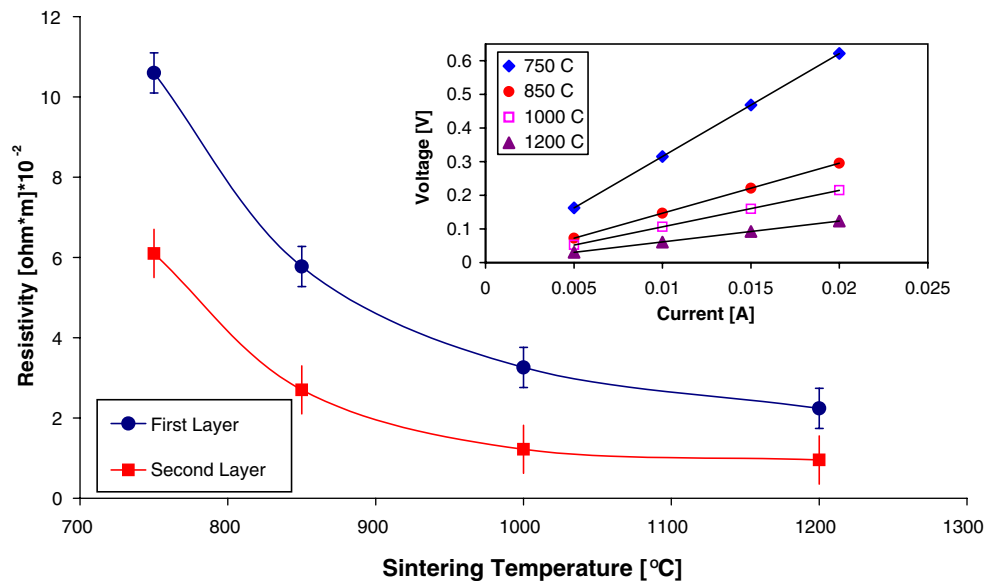


Fig. 8 Resistivity vs. carbonization temperature for one and two layers. The insert shows the IV measurement of first layer at different carbonization temperatures



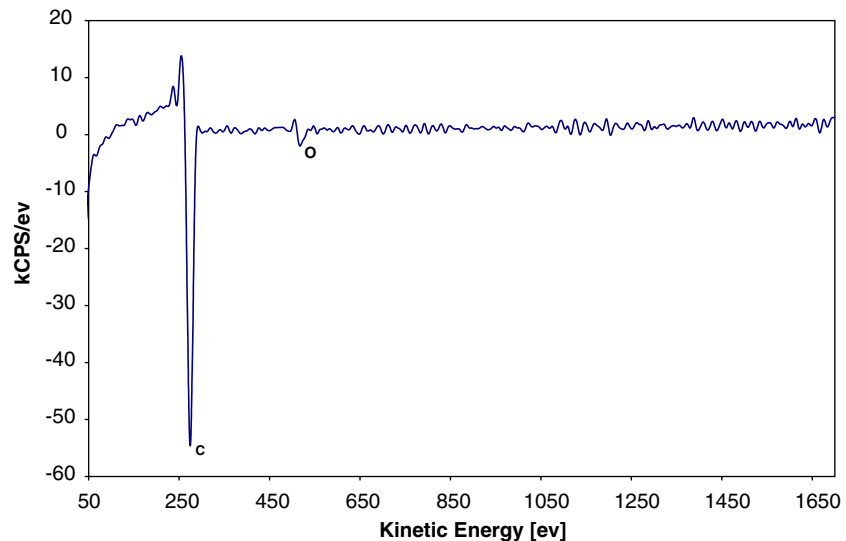
Auger signal for a typical carbon film. Our samples show approximately 96% carbon, with small amounts of oxygen on the film surface. This oxygen contamination is common for samples exposed to air due to O_2 surface adsorption [11].

μ -Raman spectroscopy

μ -Raman spectroscopy was used to characterize the phase and structure of the carbon layers. The technique

has been well documented as a reliable method for analyzing the crystal structure in pyrolytic carbon films [11–14]. Several fingerprints in the Raman spectra of pyrolytic carbon are typically used to characterize the carbon coatings. A sharp graphite (G) peak is observed at $1,580\text{ cm}^{-1}$ for single crystal graphite. It is assigned to the high frequency basal-plane stretching mode of sp^2 bonded carbon atoms. Tuinstra and Koenig [13] found a slight frequency shift toward higher wave numbers was found in some graphite samples with extremely small

Fig. 9 Auger profile of a typical carbon film. Carbon and oxygen peaks are labeled



crystal sizes. Polycrystalline graphite exhibits another peak at $1,355\text{ cm}^{-1}$, called the disorder-induced (D) peak [13].

Typical first order Raman spectra are shown in Fig. 10 for samples that were heated for 2 h at: $650\text{ }^\circ\text{C}$ (curve a), $750\text{ }^\circ\text{C}$ (b) and $1,200\text{ }^\circ\text{C}$ (c), under argon atmosphere. The spectra features carbon coatings with a well defined D and G peaks centered at approximately $1,350$ and $1,595\text{ cm}^{-1}$, respectively. All three measurements were done at identical experimental conditions. The intensities of both peaks decreased with increasing pyrolysis temperatures. This affect is attributed to the grain growth within the carbon film and diminishing grain boundary zone [13].

The most common characterization parameter is the intensity ratio $R = I_D/I_G$, which defines the level of order and the in-plane crystal size for pyrolytic graphite

films. The degree of order in graphite films is characterized by the in-plane crystal size L_a in the a -direction, and the stacking height of planes L_c , c -direction. In general, a lower R represents a high degree of order. The inverse relationship between L_a and R is shown [11, 13] in Eq. 2

$$L_a(\text{\AA}) = 44 \cdot \left(\frac{I_D}{I_G}\right)^{-1} \quad (2)$$

In the present work the ratio R as a function of the polyurethane carbonizing temperature is shown in Fig. 11. As shown, R increases while L_a decreases with temperature, respectively. The degree of disorder rises because the in-plane crystal size decreases as seen by L_a in Fig. 11. Yet the dramatic decrease in resistivity with temperature seen in Fig. 8, should be due to

Fig. 10 Raman spectra for carbon coated alumina foams at different carbonization temperatures: (a) $650\text{ }^\circ\text{C}$; (b) $750\text{ }^\circ\text{C}$; (c) $1,200\text{ }^\circ\text{C}$

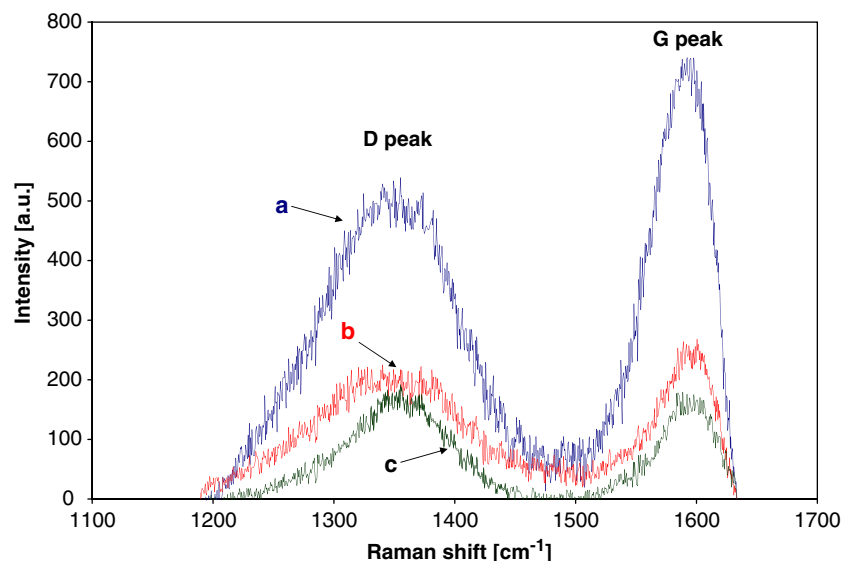
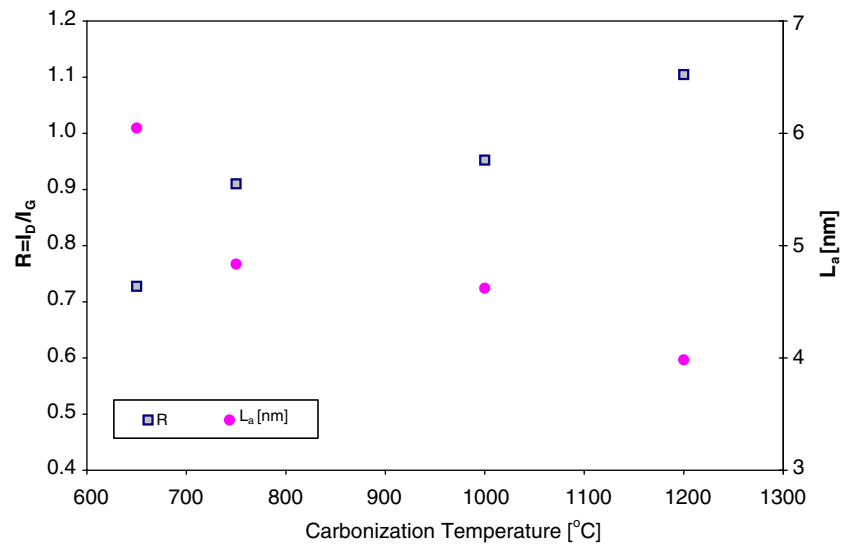


Fig. 11 Relationship of intensity ratio $R = I_D/I_G$ and crystal size L_a with carbonization temperature

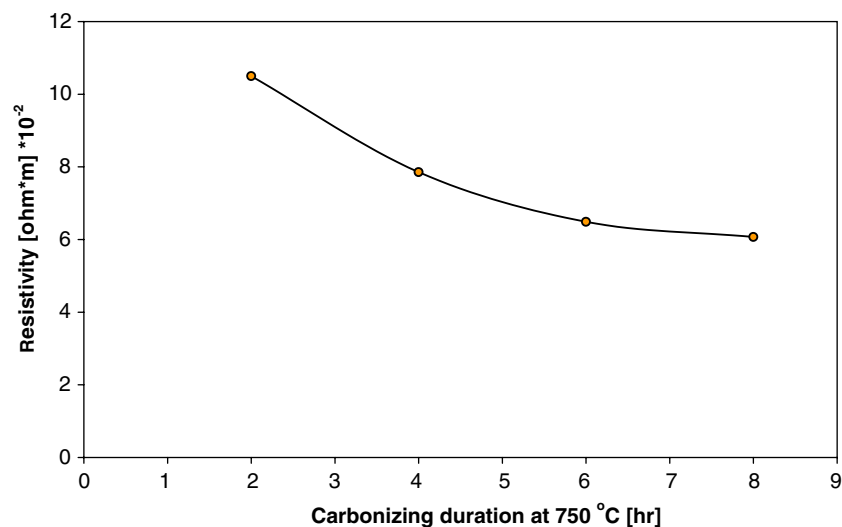


increase in the basal plane area, since the conductivity is predominately in the a -axis ($\sigma_a/\sigma_c \sim 100$) [15]. The decrease in resistivity can be explained by an increase of the stacking height (L_c), which increases the overall basal plane area and lowers the grain boundary area. The increase of L_c with temperatures is consistent with results obtained elsewhere [14]. The increase in L_c with temperature, gives rise to more ordered arrangement, which can be noticed at the thermal analysis data. As seen in Fig. 3, the wide exotherm above 700 °C, is consistent with the carbon layer development discussed above.

Effect of carbonization time

After investigating the carbonization temperature effect on the electrical conductivity, we studied the analogous effect of soaking. Five specimens, were impregnated in

Fig. 12 Resistivity vs. carbonization time, one layer, 750 °C



70% lacquer, and then soaked at 750 °C. The resistivity of each specimen was measured successively up to a total soaking time of 8 h, as shown in Fig. 12. It is evident that the resistivity drops asymptotically from 110 Ωmm to a final value of 60 Ωmm in 8 h. It can be assumed that at higher temperatures, a similar asymptotic pattern will occur, perhaps even earlier due to faster kinetics. The resistivity after 8 h soak at 750 °C is equivalent to the value obtained after 2 h soak at 850 °C (see Fig. 8). This clearly demonstrates the faster kinetics of rearrangements within the carbon film, discussed previously, at higher temperatures.

Conclusions

A method for an electronically conductive carbon coating of irregular structured bodies is presented.

In the present work, reticulated alumina foams with 80% of porosity, prepared by polymeric-sponge method, were coated with carbon by pyrolysis of a polymer layer produced by polyurethane lacquer impregnation.

The thermal behavior of polyurethane on the foam surface during pyrolysis was studied and three steps of carbon film formation were demonstrated: (a) internal chemical decomposition without weight loss, (b) thermal degradation accompanied with volatile products evolution and, (c) exothermic process of the carbon grains rearrangement followed by continuous film formation in the range of 500–950 °C. The improvement in conductivity is attributed to a rearrangement of the carbon grains on the alumina surface.

The effect of carbonizing temperature and time on the electrical conductivity, morphology and phase composition of carbon coated alumina ceramic foams was investigated in the 650–1,200 °C range in argon atmosphere. The film conductivity improved significantly with carbonization temperature and time.

Raman spectroscopy was used to measure the order (G) and disorder (D) peaks in the carbon film. The intensities ratio $R = I_D/I_G$ increased while L_a decreased with temperature, respectively. The lower resistivity at higher sintering temperatures is attributed to an overall increase in the basal plane area and lower overall grain boundary area due to increase in the stacking height L_c .

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