

Atmospheric pressure plasma assisted calcination of composite submicron fibers^{*}

Veronika Medvecká^{1,a}, Dušan Kováčik^{1,2}, Zlata Tučeková¹, Pavol Ďurina¹, Anna Zahoranová¹, and Mirko Černák^{1,2}

¹ Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University in Bratislava, Mlynská dolina F2, 842 48 Bratislava, Slovak Republic

² CEPLANT, Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

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Abstract. The plasma assisted calcination of composite organic/inorganic submicron fibers for the preparation of inorganic fibers in submicron scale was studied. Aluminium butoxide/polyvinylpyrrolidone fibers prepared by electrospinning were treated using low-temperature plasma generated by special type of dielectric barrier discharge, so called diffuse coplanar surface barrier discharge (DCSBD) at atmospheric pressure in ambient air, synthetic air, oxygen and nitrogen. Effect of plasma treatment on base polymer removal was investigated by using Attenuated total reflectance – Fourier transform infrared (ATR-FTIR) spectroscopy. Influence of working gas on the base polymer reduction was studied by energy-dispersive X-ray spectroscopy (EDX) and CHNS elemental analysis. Changes in fibers morphology were observed by scanning electron microscopy (SEM). High efficiency of organic template removal without any degradation of fibers was observed after plasma treatment in ambient air. Due to the low-temperature approach and short exposure time, the plasma assisted calcination is a promising alternative to the conventional thermal calcination.

1 Introduction

Aluminium dioxide/alumina (Al_2O_3) is one of the most widely used functional ceramic material finding application in many fields of industry attributed to its high heat and corrosion resistance, chemical stability, low thermal conductivity and good electrical insulation. Alumina 1-D structure has great importance in advanced applications such as heat engine, aerospace, gas sensors, catalysis, filtration, etc. [1, 2]. These structures are usually prepared by sol-gel, hydrothermal, solvothermal methods and others [3–7]. Usage of electrospinning extended the concept of fibers fabrication from polymer solution by preparation of inorganic fibers in submicron scale [8–12]. In this process the polymer solution is enriched by precursor – substance containing inorganic part. Subsequently the obtained composite fibers are calcined at high temperature to remove polymer template and transform the composite fibers into inorganic fibers. The significant disadvantages of thermal calcination besides the high temperature and long calcination time (500–1000 °C for 5–10 h) are high volume losses of material causing the

breakdown of the fibers, necessity of thermal stable substrate and oxidation of the substrate and thereby reducing the adhesion of nanofibers on the substrate. Thermal calcination is due to the energy and time consumption considerably very expensive process.

The plasma assisted calcination provides a promising low-temperature, low-cost and time-saving method for preparation of inorganic fibers. The low temperature, non-equilibrium plasma generated in working gas with oxidative effect, e.g., oxygen and air, appears to be a suitable tool for the oxidation and removing of organic base polymer at low temperature by active oxygen species produced in plasma. This type of plasma, generated at low or atmospheric pressure has already been used for plasma calcination by producing nanopowders, inorganic thin layers and inorganic fibers [13–16].

In present work we used for plasma assisted calcination of the composite aluminium butoxide/polyvinylpyrrolidone fibers the atmospheric pressure plasma generated by diffuse coplanar surface barrier discharge (DCSBD) [17, 18] in various gases. This type of plasma source has already been successfully used for atmospheric pressure plasma assisted calcination of ceria fibers [19]. High power density of generated plasma (100 W/cm^3) results in short exposure times [20]. The main advantage of DCSBD discharge is operation in

^a e-mail: veronika.medveckova@fmph.uniba.sk

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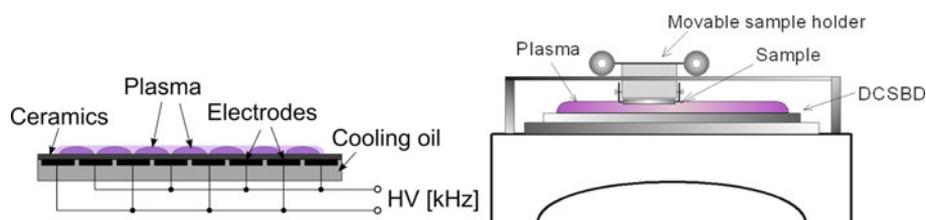


Fig. 1. Schematic drawing of DCSBD discharge and experimental apparatus for plasma treatment of fibers.

diffuse mode at atmospheric pressure in any working gas (even electronegative, e.g., oxygen) to prevent degradation of fibers due to the filamentary character of conventional DBD plasma sources.

2 Experimental

2.1 Samples

Precursor/polymer composite fibers for preparation of inorganic submicron fibers were prepared by electrospinning from solution of aluminium butoxide and polyvinylpyrrolidone (Al(Bu)/PVP) on glass microscope slide. Composite fibers and alumina fibers prepared by conventional thermal calcination were provided by Pardam Nanotechnology Ltd, Czech Republic.

2.2 Plasma treatment

Composite fibers were treated by atmospheric pressure plasma generated by diffuse coplanar surface barrier discharge (DCSBD) detailed described in references [17, 18, 21, 22]. Plasma treatment of samples was realized at atmospheric pressure in ambient air, synthetic air (N₂:O₂ 80%:20%), oxygen and nitrogen in a continuous flow mode with gas flow rate 5 L/min. The distance between the sample and planar ceramic plate of DCSBD was fixed to 0.3 mm by the moveable sample holder (Fig. 1). The plasma exposure time was in the range of 1–60 min at input power 400 W.

2.3 Diagnostic methods

Gravimetric measurement was performed using analytical balances KERN ABT 220-4 M (Kern&Sohn GmbH, Germany). Attenuated total reflectance – Fourier transform infrared (ATR-FTIR) spectroscopy spectra were obtained using Bruker Vector 22 FT-IR spectrometer with additional accessories Pike MIRacle™ in the range of 4500–500 cm⁻¹ during 20 scans, with 2 cm⁻¹ resolution using diamond crystal. Morphology of fibers before and after plasma treatment was studied by *scanning electron microscope* Vega II SBH (Tescan, CZ) at accelerating voltage 30 kV, current flow 20 pA and working distance of 4 mm. *EDX measurements* were realized using Vega I TS 5136 MM (Tescan, CZ) with EDX spectrometer INCA

x-sight (Oxford Instruments, UK). Samples for SEM and EDX measurements were coated with the 20 nm thin gold layer by SEM coating system (BIO-RAD E52-5199) at pressure 8 Pa in argon. *CHNS analysis* was performed using Vario El III CHNOS elemental analyzer (Elementar Analysensysteme Ltd, Germany) at the temperature of 1200 °C. Accuracy of the method was determined by manufacturer of device for analysis of 5 mg standard of 4-aminobenzensulfonic acid in CHNS mode to <0.1% abs. for each element.

3 Results and discussion

Gravimetric measurement provides immediate quantification of the samples weight changes before and after plasma calcination due to the degradation of organic polymer and unwanted part of precursor. The changes in the weight of Al(Bu)/PVP composite fibers in dependence on the exposure time in plasma are shown in Figure 2. The decrease in weight indicates exponential decay. The strongest effect of DCSBD plasma on reduction of base polymer was observed in first 10 min.

ATR-FTIR spectroscopy was used to identify the changes in chemical bonds on composite fibers before and after plasma treatment causing weight losses. ATR-FTIR spectrum of the reference sample, samples after 10 and 30 min of plasma treatment and thermally calcined sample are shown in Figure 3.

In the spectrum of reference Al(Bu) + PVP sample, the characteristic functional groups of polyvinylpyrrolidone can be observed in the region 1200–1700 cm⁻¹. The pronounced intensity peaks, typical for PVP, attributed to stretching vibration of carboxyl group C=O at 1640–1680 cm⁻¹, deformation vibration of C-H at 1380–1490 cm⁻¹ and stretching vibration of C-N at around 1290 cm⁻¹ can be visible in spectrum of the reference sample [23–25]. After plasma calcination the strong decline in intensity of characteristic peaks for PVP can be detected. Asymmetric and symmetric stretching vibration of C-H can be visible at 2920–2980 cm⁻¹ and 2840–2900 cm⁻¹, respectively [24, 26, 27]. This peak completely disappears after 30 min of plasma treatment. In the region 3000–3500 cm⁻¹ decline of O-H band from absorbed water on material is observed [23, 24, 27]. Vibrations of chemical bonds in precursor contribute to the intensity of the peaks attributed to PVP on reference sample. In the spectra, stretching and bending vibration of C-H from methylene groups (CH₂) in aluminium butoxide can be visible at

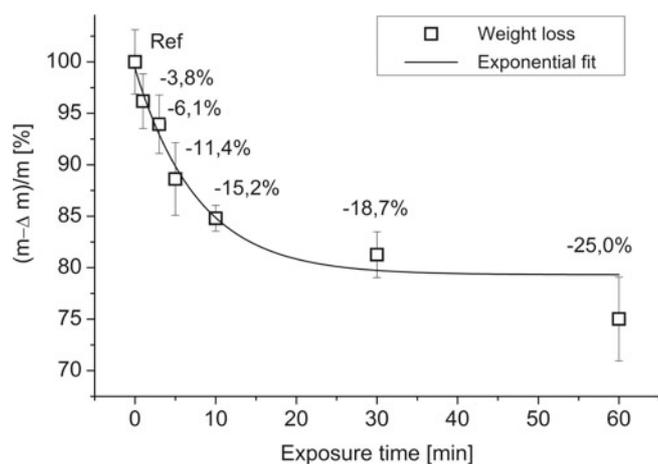


Fig. 2. Weight losses of Al(Bu)/PVP samples after plasma treatment in dependence on exposure time. Plasma treatment realized in ambient air at input power 400 W and distance 0.3 mm.

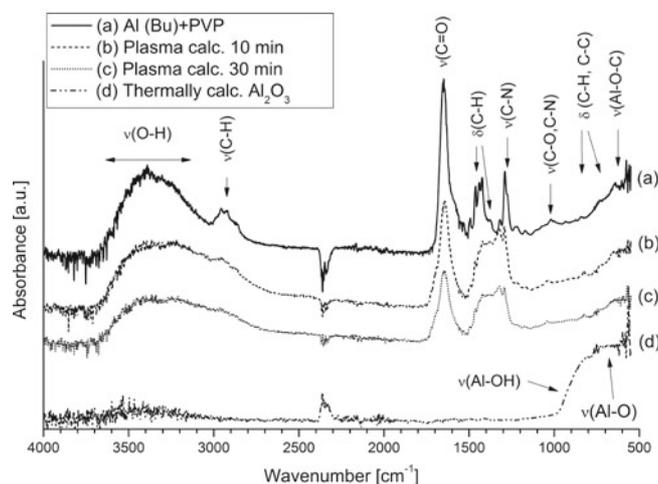


Fig. 3. ATR-FTIR spectra of Al(Bu)/PVP fibers before and after plasma calcination in ambient air at exposure time of 10 and 30 min and thermally calcined sample.

2850–2950 cm^{-1} and 1350–1600 cm^{-1} , respectively [26,28]. Vibrations of Al-O bond in aluminium oxide located at around 600 cm^{-1} are visible in the spectrum of thermally calcined sample [28,29]. In the region 2300–2400 cm^{-1} can be seen peaks attributed to CO_2 molecule coming from ambient air or residues formed during oxidation of organics. However, in region 1900–2300 cm^{-1} the sensitivity of diamond crystal is decreased.

Figure 4 shows the atomic ratio of carbon, oxygen and nitrogen to aluminium measured by *EDX spectroscopy* on the reference sample, samples treated by the DCSBD plasma for 10 and 30 min in ambient air, synthetic air, oxygen and nitrogen.

The plasma calcination in laboratory air, oxygen and nitrogen after 10 min of exposure time leads to a similar reduction of atomic ratio of C/Al (36%, 37% and 39%, respectively). After 30 min of plasma treatment the

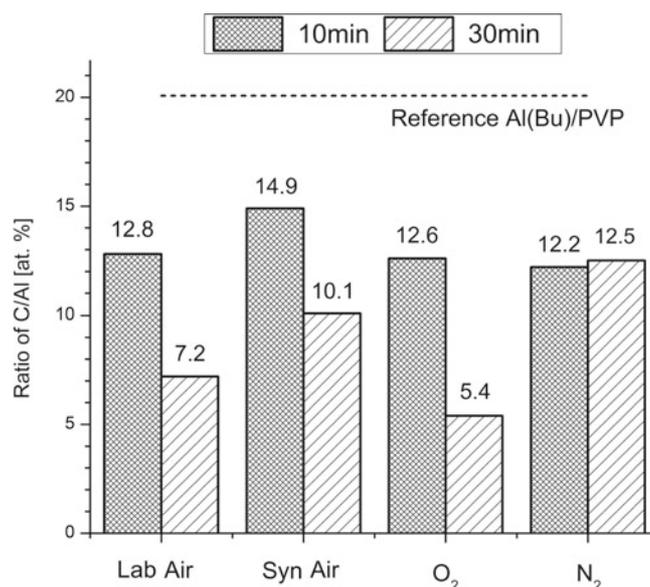


Fig. 4. Comparison of atomic ratio of C/Al in sample of Al(Bu)/PVP fibers after the plasma calcination at exposure time of 10 and 30 min in different working gases.

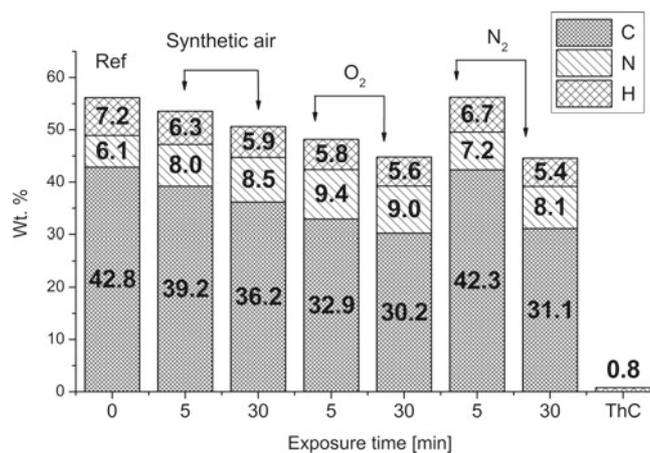


Fig. 5. CHNS analysis. Content of total carbon, nitrogen and hydrogen in samples of Al(Bu)/PVP fibers before and after plasma calcination at exposure time of 5 and 30 min in different gases.

reduction of C/Al ratio in nitrogen is unchanged while in laboratory air and oxygen decreased by 64% and 73%. Oxygen as a strong oxidizing agent can effectively decompose the organics of the base polymer. Higher activity of the base polymer removal during the plasma calcination in ambient air compared to synthetic air can be related to the presence of air humidity. OH radicals generated in plasma in the atmosphere with water vapour play an important role during the oxidation and decomposition of the organic part of the composite fibers.

CHNS analysis provided information about the content of total carbon, hydrogen, nitrogen and sulphur in samples. Figure 5 depicts the composition of Al(Bu)/PVP samples treated with plasma generated by the DCSBD in synthetic air, oxygen and nitrogen after 5 and 30 min of

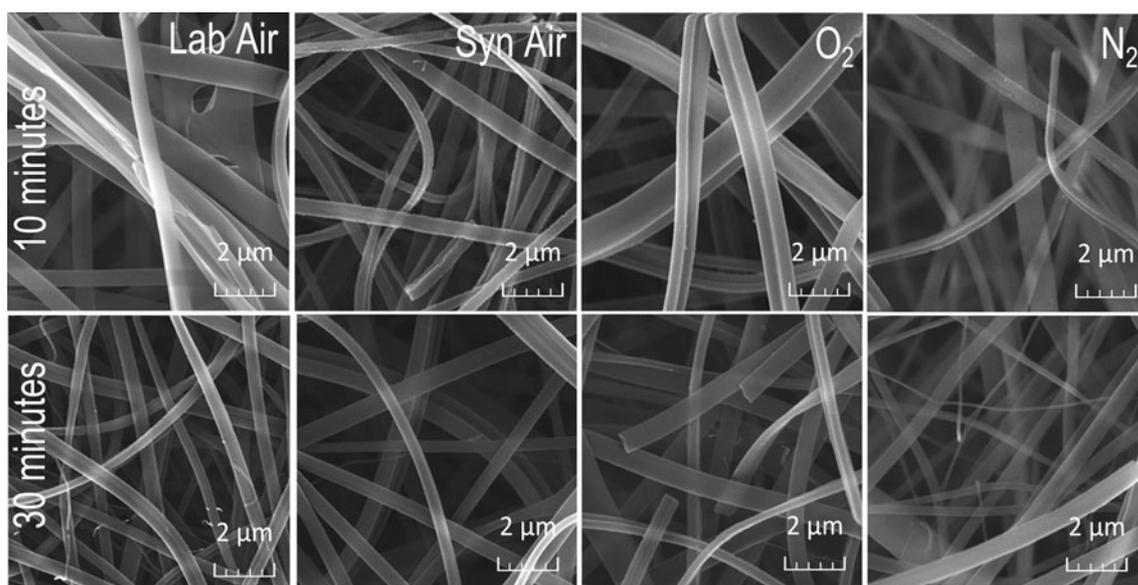


Fig. 6. SEM micrographs of Al(Bu)/PVP fibers samples treated for 10 and 30 min in ambient air, synthetic air, oxygen and nitrogen. Magnification of 20 kx.

plasma treatment. A significant reduction in carbon content was recorded after the plasma treatment in oxygen due to its high oxidation potential. The lowest effect on the organics removal from fibers was observed in synthetic air. While EDX measurements provide information about the surface of samples (penetration depth is in the order of few microns), CHNS analyses the composition of the whole samples and we can compare efficiency of active particles transfer through the sample. As we can see at Figure 5, plasma treatment in synthetic air has low efficiency to penetrate through the material.

SEM micrographs of samples treated by the DCSBD plasma for 10 and 30 min in ambient air, synthetic air, oxygen and nitrogen are shown in Figure 6. Samples treated for 30 min in the oxygen evinced breaking of the fibers. Degradation of structure can be caused by strong removal of the material observed by elemental analysis. Plasma treatment in ambient air, synthetic air and nitrogen does not cause damage of fibrous structure.

4 Conclusion

Plasma assisted calcination is attractive due to the low temperature approach compared to the conventional long-term thermal calcination. Diffuse character and macroscopically homogeneous plasma generated in thin layer is applicable for the treatment of fibers in the submicron range without the damage of their structure. In contrast to other types of plasma sources, where the uniformity of plasma is achieved by low pressure or working gases inhibiting the oxidation activity of plasma (nitrogen, argon, etc.), DCSBD enables continuous treatment of samples without the use of vacuum devices and maintains high ratio of diffuse plasma without the need of any working gas or even in gases with high oxidation potential. The plasma assisted calcination can be a low

temperature alternative to the annealing to prepare fibers for application, where the complete removal of organics is not necessary or as a pre-treatment method for shorten of process and reduction of calcination temperature.

Efficiency of plasma assisted calcination using diffuse coplanar surface barrier discharge in different gases depends on ability of active species produced in plasma to decompose the base polymer and residues from precursor. Despite the fact, that oxygen plasma generated by DCSBD was very efficient in reduction of carbon, the strong removal of polymer template in oxygen can cause degradation of fibrous structure. The results obtained from the plasma treatment by DCSBD in ambient air showed the effective removal of organics without any degradation of fibrous structure. Plasma treatment without the need of any working gas is very prospective for application of plasma assisted calcination using DCSBD in the practice.

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References

1. X. Liu, Z. Wu, T. Peng, P. Cai, H. Lv, W. Lian, Mater. Res. Bull. **44**, 160 (2009)
2. D. Yang, B. Paul, W. Xu, Y. Yuan, E. Liu, X. Ke, R.M. Wellard, C. Guo, Y. Xu, Y. Sun, H. Zhu, Water Res. **44**, 741 (2010)
3. M. Noordin, K. Liew, in *Nanofibers*, edited by A. Kumar (InTech, 2010), pp. 405–418
4. J. Wang, Y. Wang, M. Qiao, S. Xie, K. Fan, Mater. Lett. **61**, 5074 (2007)

5. G.L. Teoh, K.Y. Liew, W.A.K. Mahmood, J. Sol-Gel Sci. Technol. **44**, 177 (2007)
6. J.A. Muñoz-López, J.A. Toledo, J. Escobar, E. López-Salinas, Catal. Today **133–135**, 113 (2008)
7. B. Guo, H. Yim, Z.P. Luo, J. Aerosol Sci. **40**, 379 (2009)
8. A.-M. Azad, Mater. Sci. Eng. A **435–436**, 468 (2006)
9. A. Mahapatra, B.G. Mishra, G. Hota, Ceram. Int. **37**, 2329 (2011)
10. V. Maneeratana, W.M. Sigmund, Chem. Eng. J. **137**, 137 (2008)
11. K. Nakane, M. Seto, S. Irie, J. Appl. Polym. Sci. **121**, 1774 (2011)
12. P.K. Panda, S. Ramakrishna, J. Mater. Sci. **42**, 2189 (2007)
13. J.M. Gomez-Vega, K. Teshima, A. Hozumi, H. Sugimura, O. Takai, Surf. Coat. Technol. **169–170**, 504 (2003)
14. Z. Károly, J. Szépvölgyi, Z. Farkas, Powder Technol. **110**, 169 (2000)
15. P. Baroch, J. Hieda, N. Saito, O. Takai, Thin Solid Films **515**, 4905 (2007)
16. H. Wang, H. Tang, J. He, Q. Wang, Mater. Res. Bull. **44**, 1676 (2009)
17. M. Šimor, J. Ráhel', P. Vojtek, M. Černák, A. Brablec, Appl. Phys. Lett. **81**, 2716 (2002)
18. M. Černák, D. Kováčik, J. Ráhel', P. St'ahel, A. Zahoranová, J. Kubincová, A. Tóth, L. Černáková, Plasma Phys. Control. Fusion **53**, 124031 (2011)
19. V. Medvecká, D. Kováčik, A. Zahoranová, M. Stupavská, M. Černák, Mater. Lett. **162**, 79 (2016)
20. D. Skácelová, V. Danilov, J. Schäfer, A. Quade, P. St'ahel, M. Černák, J. Meichsner, Mater. Sci. Eng. B **178**, 651 (2013)
21. M. Černák, L. Černáková, I. Hudec, D. Kováčik, A. Zahoranová, Eur. Phys. J. Appl. Phys. **47** (2009)
22. T. Homola, J. Matoušek, V. Medvecká, A. Zahoranová, M. Kormunda, D. Kováčik, M. Černák, Appl. Surf. Sci. **258**, 7135 (2012)
23. Q. Cui, X. Dong, J. Wang, M. Li, J. Rare Earths **26**, 664 (2008)
24. A.M. Abdelghany, E.M. Abdelrazek, D.S. Rashad, Spectrochim. Acta A: Mol. Biomol. Spectrosc. **130**, 302 (2014)
25. M.I. Loría-Bastarrachea, W. Herrera-Kao, J.V. Cauich-Rodríguez, J.M. Cervantes-Uc, H. Vázquez-Torres, A. Ávila-Ortega, J. Therm. Anal. Calorim. **104**, 737 (2011)
26. D.W. Mayo, F.A. Miller, R.W. Hannah, *Course Notes on the Interpretation of Infrared and Raman Spectra* (John Wiley & Sons, Inc., Hoboken, NJ, USA, 2003)
27. M. Şen, E.N. Avci, J. Biomed. Mater. Res. – Part A **74**, 187 (2005)
28. S. Lukić, I. Stijepović, S. Ognjanović, V.V. Srdić, Ceram. Int. **41**, 3653 (2015)
29. A. Beran, D. Voll, H. Schneider, J. Eur. Ceram. Soc. **21**, 2479 (2001)