# INVESTIGATION OF ATMOSPHERIC PRESSURE PLASMA SURFACE MODIFIED ALUMINIUM OXIDE NANOPOWDER BY THERMAL DESORPTION SPECTROSCOPY

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**Abstract**

Aluminium oxide nanopowder is used for sintering into ceramic materials with attractive mechanical properties. The simplest and most common sintering methods are wet methods during which the nanopowder is dispersed in a liquid. High surface energy increases the quality of the sintered material. Atmospheric pressure plasma is known improve its wetting properties and the quality of ceramic sintered using the electrophoretic method. However, polarisation abnormalities during the deposition suggested an addition of negatively charged species on the powder's surface during the treatment, probably $NO_X$ molecules. To verify this hypothesis, we have used the Thermal Desorption Spectroscopy on the treated and the untreated nanopowder to study the changes that occurred during the treatment. We have found that a large number of additional NO, $NO_2$, $CO_2$ and hydroxyl were attached to the surface, at least some of them were grafted rather than adsorbed. This provided additional evidence that the abnormalities were caused by $NO_X$ molecules on the surface.

**Keywords:** Alumina, sintering, electrophoretic method, plasma treatment, Thermal Desorption Spectroscopy

## 1. INTRODUCTION

Aluminium oxide is a material with many useful properties, such as high hardness, high wear resistance, corrosion resistance, thermodynamic stability and can also have good transparency. It has a lot of application in cutting tools, optical objects, implants etc. [1]

Alumina ceramic's properties are improved with smaller grain size of the material it's sintered from, changing significantly as the grains reach the nanoscale. Such materials are made of nanopowders via sintering. These methods also allow mixing more types of nanopowders together to create nanocomposite materials [2].

Electrophoretic deposition is a cost-effective and versatile sintering method. This method requires a high concentration suspension of the nanopowder in a liquid, otherwise particles deposit at different speeds [3]. Hydrophilicity of the nanopowder helps ensure good mixing of the powder in the liquid and thus increase the quality of the sintered material.

Tomáš Morávek and colleagues have verified that plasma treatment in DCSBD reduces the surface roughness and slightly improves the density and grain size of electrophoretically sintered coatings [4]. XPS measurements had shown an increased amount of C-O bonds and AlOOH bonds. However, while investigating the behaviour of plasma treated and as-received aluminium oxide powders during the electrophoretic deposition, it was discovered that the main difference between the processes is a change of the polarization of the electrode where the deposit was created. The plasma treated powders created the deposit on the positive electrode while the deposit created from the suspension containing non-treated powder was formed on the negative electrode. To be possible for this to happen, some negatively charged species had to be adsorbed on the powder's surface during the treatment. By using different analytical methods, it was concluded that one of possible causes is an adsorption of $NO_X$ molecules.

In order to investigate if there were any $NO_X$ gases, we have analysed the result using Thermal Desorption Spectroscopy (TDS) [5] on alumina nanopowders before and after treatment with a Diffuse Coplanar Surface Barrier Discarge (DCSBD) [6]. We have compared the results to data obtained from FTIR.

## 2. EXPERIMENTAL

We have used high-purity (99.99 %) Taimicon TM-DAR nanopowder from company Taimei chemicals with grain size 0.1 μm. According to the manufacturer, the powder's surface is 14.5 $m^2/g$.

We have used a DCSBD discharge with area 196 x 78 mm, containing two electrodes of interlocking comb pattern with 30 stripes placed 1 mm apart from each other (**Figure 1**). We have placed the nanopowder on the discharge's surface with homogeneous width. The experiment was performed in air at atmospheric pressure. The discharge was fed by 500 W power with frequency 30 kHz. The process lasted for 30 seconds.

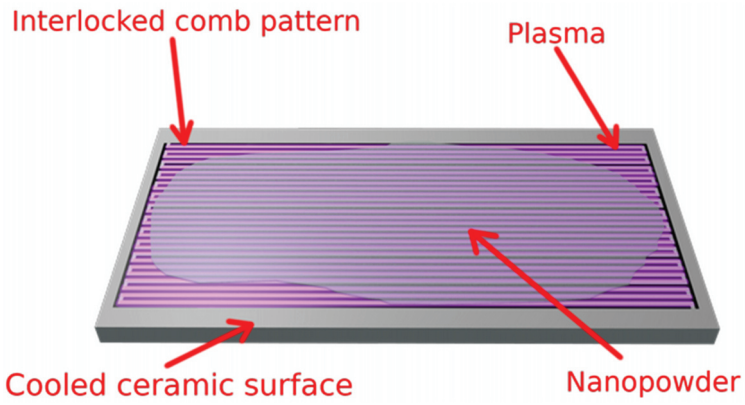


**Figure 1** Using a DCSBD to process the nanopowder

The Thermal Desorption Spectroscopy measurement was performed on a custom-built device (**Figure 2**). About 300 mg of the nanopowder was placed in a metal vessel and inserted into a vacuum chamber evacuated by a Pfeiffer D-35614 Asslar turbomolecular pump, at high vacuum at pressure around $5 \cdot 10^{-5}$ Pa. Using a Clasic laboratory fournace, the powder was heated by 10K/min until temperature 1000 °C and kept at 1000 °C for 30 min. Mass spectra of gases desorbed during the reactions caused by increasing temperature were measured using a Prisma 80 quadrupole mass spectrometer from Pfeiffer with range from 1 to 80 amu. Results were computed and visualised using a custom program developed with Qt.

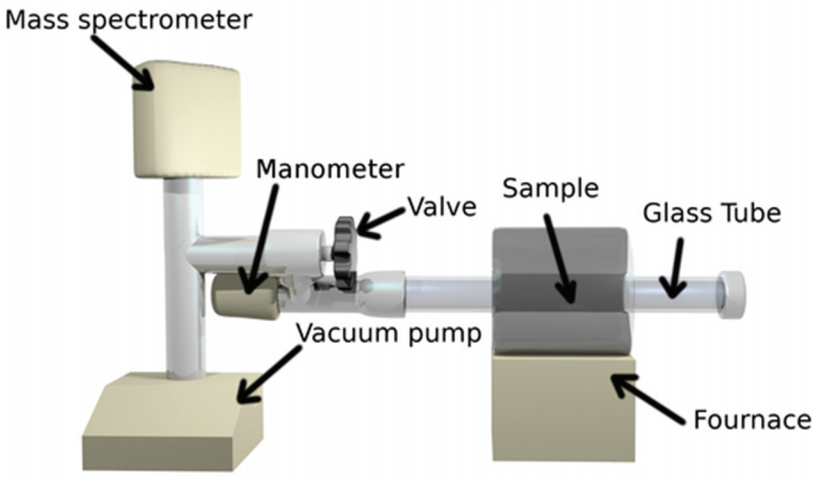


**Figure 2** The apparatus used for TDS

## 3. RESULTS AND DISCUSSION

First, we have measured thermal desorption spectra of treated and untreated nanopowder at temperatures up to 1000 °C. The data were rendered into a heatmap where every point's colour indicates the amount of desorbed gas of mass determined by its x position at temperature determined by its y position (**Figure 3**).

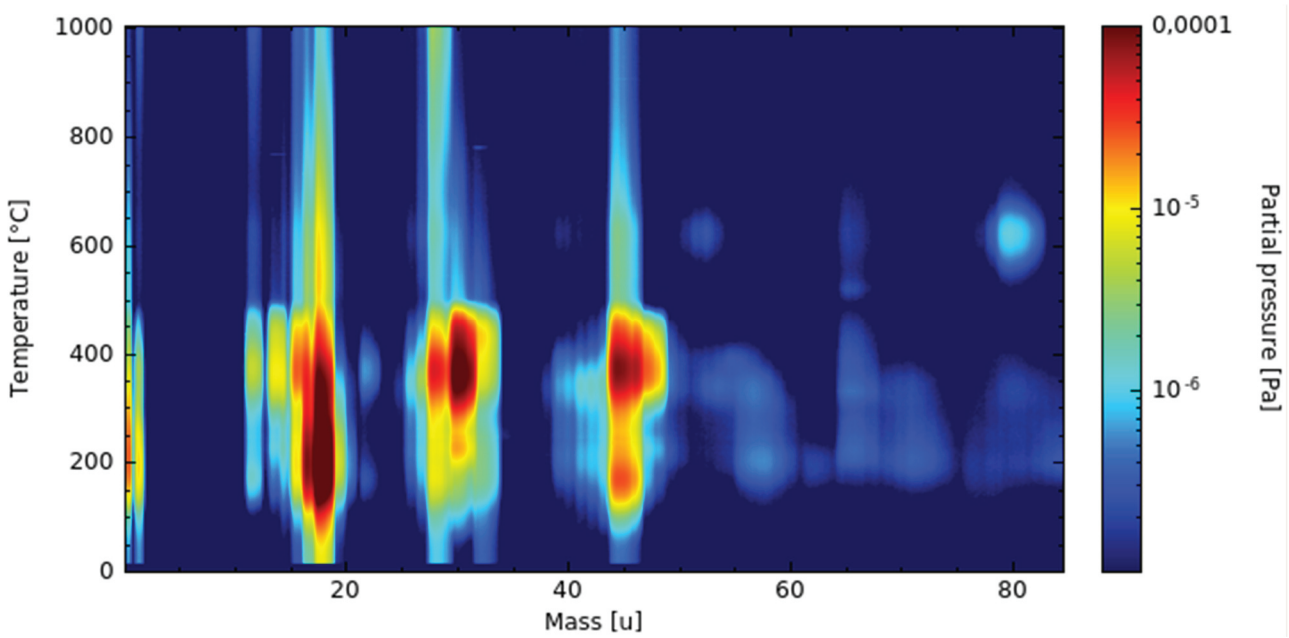


**Figure 3** Thermal Desorption heatmap of plasma-treated alumina nanopowder

We can see a large desorption peak of water around temperature 200 °C. There are also desorption peaks of other materials at that temperature, especially oxygen, nitrogen and carbon dioxide. There is also a desorption maximum around temperature 380 °C, especially for oxygen, nitrogen, nitrogen dioxide and carbon dioxide. The data from untreated powder are in the following heatmap: Then, we treated the nanopowder with DCSBD plasma for 30 s and measured its effects on the spectra (**Figure 4**).

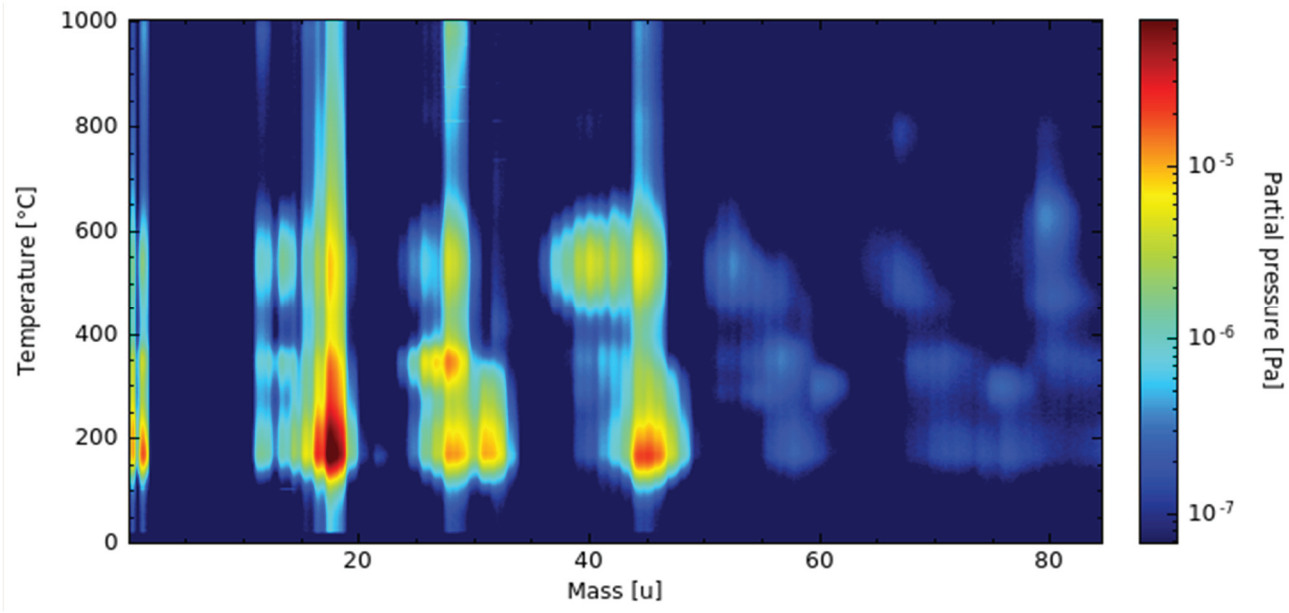


**Figure 4** Thermal Desorption heatmap of untreated alumina nanopowder

Besides the large desorption peak around temperature 200 °C, we can see a smaller group of desorption peaks of oxygen and nitrogen around temperature 400 °C. The series of small peaks released at temperature around 500 °C appeared also in experiments without the nanopowder. Therefore, the plasma treatment greatly affected the peak appearing at temperature 380 °C. Graph at **Figure 5** shows this release more closely to

allow to determine which gases were released and their relative amounts compared to the release from untreated sample.

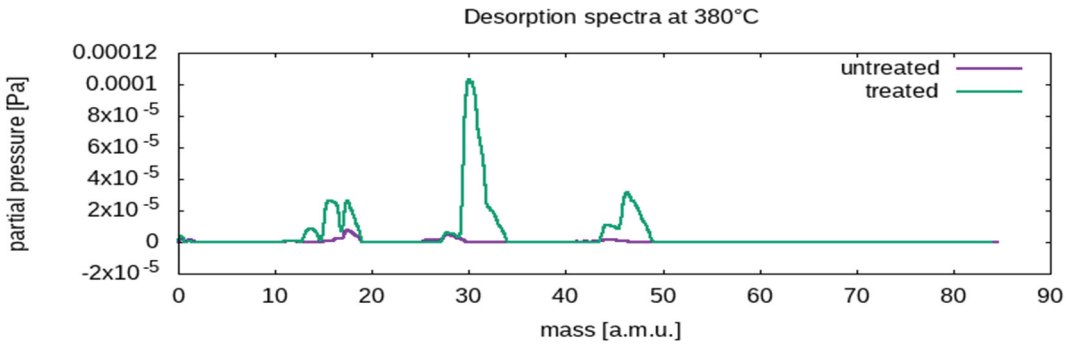


**Figure 5** TDS spectrum at temperature 380 °C

In the spectra of the untreated nanopowder, we can see mostly atmospheric gases and water vapour, which may originate from the vacuum chamber's walls. In the spectra of the plasma-treated nanopowder, there is a large additional release at masses 14, 16, 17, 18, 30 32, 44 and 46 u (**Table 1**).

**Table 1** Probable species corresponding to the desorbed masses

| Mass | Probable species |
|---|---|
| 14 | N (fragment of $N_2$, NO or $NO_2$) |
| 16 | O (fragment of $O_2$, NO, $NO_2$ or $H_2O$) |
| 17 | OH |
| 18 | $H_2O$ |
| 30 | NO |
| 32 | $O_2$ |
| 44 | $CO_2$ |
| 46 | $NO_2$ |

It is unlikely that species at masses 30 and 44 were ethane and propane respectively because of the absence of fragments that are typical for hydrocarbons. The massive releases at masses 30 and 46 corresponding to nitrogen oxide and nitrogen dioxide suggest that the sample indeed contains $NO_X$ as hypothetised.

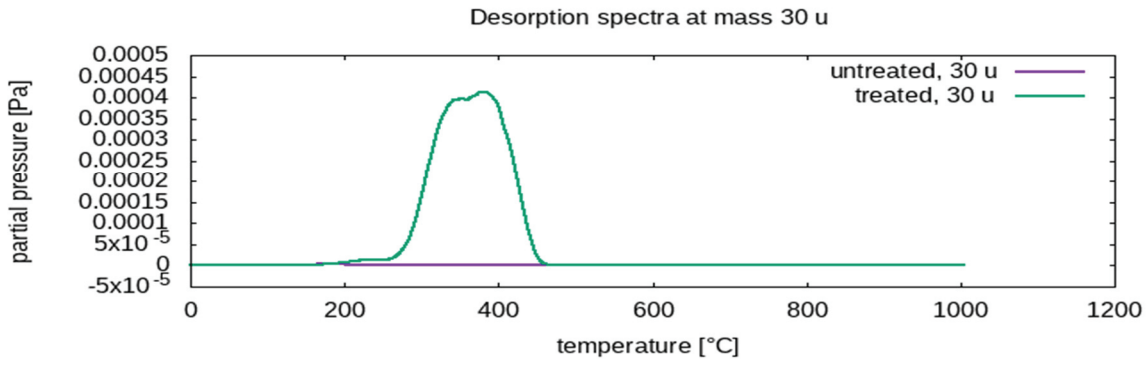


**Figure 6** TDS trends of species at mass 30 u

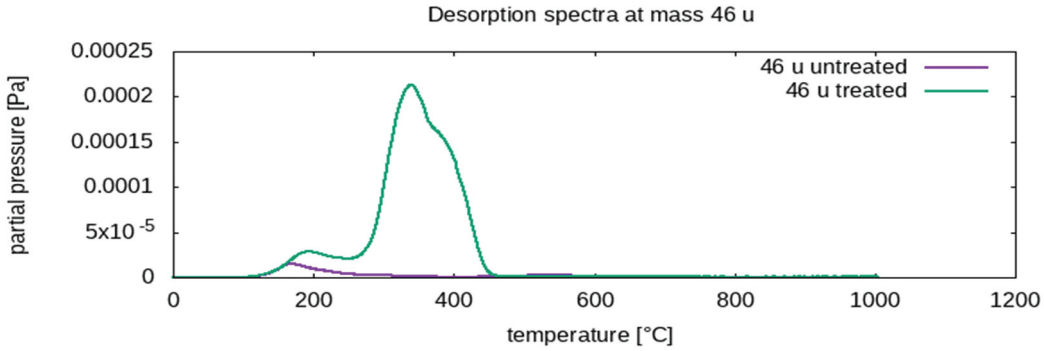


**Figure 7** TDS trends of species at mass 46 u, corresponding to nitrogen dioxide

The trends at masses 30 u and 46 u (**Figures 6 and 7**) give strong evidence that the plasma-treated samples contain much larger amounts of $NO_X$. We can also observe an additional peak in the data from the treated sample that did not appear in the data from the untreated sample. Therefore, the nitrogen oxides are also bonded differently in the treated sample.

To determine if these new species were grafted to the surface or adsorbed from the surrounding atmosphere, we have used a FTIR measurement. We were able to identify some of the detected species and determine how did their amount change during the plasma treatment (**Table 2**).

**Table 2** Changes in concentrations of species detected by FTIR

| Species | Change |
|---|---|
| hydroxyl | substantial increase |
| adsorbed $H_2O$ | removed |
| possibly $NO_X$ | increase |
| $CH_X$ | removed |
| $Al_2O_3$ | unchanged |

The replacement of adsorbed water with hydroxyl groups suggests that the treatment grafted new functional groups to the nanopowder's surface. Unfortunately, we could not determine if the $NO_X$ was grafted or adsorbed to the surface.

While both TDS and FTIR measurements confirm that the amount of $NO_X$ increased during the treatment, neither allowed us to determine if it was grafted or adsorbed. This might be possible to decide by modelling the peaks and determining their activation energy and decide if they were grafted or adsorbed, but it is a challenging task because the peaks appear to be composed of two individual reactions culminating at similar temperatures.

## 4. CONCLUSION

We have measured the Thermal Desorption Spectra of untreated alumina nanopowder and of alumina nanopowder treated by DCSBD plasma. The results show that the chemical properties of the nanopowder surface were significantly altered. The plasma modified surface contained additional functional groups, either able to capture or consisting of additional oxygen, hydroxyl, nitrogen monoxide, nitrogen dioxide and carbon dioxide. This provides additional evidence to an earlier hypothesis that nitrogen oxides were added to the nanopowder's surface during the treatment. Further analysis has shown that some of the species were grafted at the surface, but we were not able to determine how were the nitrogen oxides attached to the surface. Additional modelling of the thermal desorption process might determine the nature of the attachment.

## ACKNOWLEDGEMENTS

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