A LUMINESCENCE STUDY OF PLASMA TREATED ALUMINA POWDERS

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Abstract

The sintering of plasma pre-treated alumina sub-micron powders results in finer microstructure of final ceramics. This highly interesting and potentially useful result motivates us to study the microscopic changes on plasma treated alumina powders. In this paper we present the study of luminescence produced by thermally stimulated plasma treated alumina powders, to extend the portfolio of standard surface diagnostic tools specializing primarily at chemical and topological changes. We found that luminescence signal is exceedingly sensitive to plasma treatment. The comprehensive set of experiments implies that the emitted light is produced chiefly by the process of thermoluminescence. Hence the emitted light is the direct consequence of plasma assisted electron trapping in the material, rather than the outcome of chemical reactions.

Keywords: alumina, DCSBD, thermoluminescence, sub-micron powder

1. INTRODUCTION

Our previous work had shown that plasma pre-treatment of alumina powder has a positive effect on the microstructure of resulting sintered ceramics [1]. Standard set of surface diagnostic techniques (FTIR, Raman, XPS, SEM) were used to identify the novel chemical groups introduced to powder surface by plasma, which may be responsible for the effect. Nevertheless one must bear in mind, that chemical changes (detectable by these techniques) may have only limited influence on the processes taking place at very high temperatures required for ceramics sintering (1200 - 1600°C). It is therefore of interest to extent the so far used surface diagnostic technique by measurements of thermally stimulated light emission of plasma treated samples, which can be attributed either to chemiluminescence (CL) or to thermoluminescence (TL) effect

Chemiluminescence accompanies certain types of exothermic chemical reactions, usually of oxidative nature. It is commonly used for the detection of traces of hydrogen peroxide [2] and monitoring the oxidation stability of polymers [3,4,5]. The measurements of chemiluminescence (CL) typically consists of heating the substrate (isothermally or with steadily increasing temperature) followed by the detection of spectrally unresolved light. Thermoluminescence (TL) caused by thermal detrapping of electrons accompanied by emission of light can also play an important role. The TL phenomenon is frequently employed in dosimetric applications [7,8]. The specific feature of TL is that its presence cannot be detected by above mentioned standard set of surface diagnostic tools (i.e. FTIR, Raman, XPS, SEM). The aim of this work is to identify the magnitude and main contributor to the detected thermally induced light emission.

2. EXPERIMENTAL

2.1. Plasma source

Non-thermal plasma generator of Diffuse Coplanar Surface Barrier Discharge (DCSBD - Fig. 1) was used for plasma treatment of alumina sub-micron powder. It consisted of a screen-printed array of coplanar strip-like electrodes (1.5 mm electrode width, 1 mm inter-electrode spacing) on the bottom side of a 96% purity Al_2O_3

plate with the thickness of 0.6 mm.. The active plasma area of DCSBD unit was 8×20 cm^2. The electrode was cooled by circulating transformer oil, which also provides an additional electrical insulation. The system was powered by 14 kHz sinusoidal high-voltage of up to 20 kV peak-to-peak amplitude. By increasing the driving voltage, a thin layer (about 0.3 mm) of low temperature non-equilibrium plasma consisting of H-shaped microdischarges emerges on the upper surface of the ceramics plate [9].

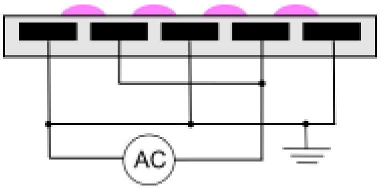


Fig. 1 Schematics of DCSBD setup. Only a reduced number of electrodes is shown for the sake of clarity.

2.2. Material

Plasma treatment was carried out on the sub-micron alumina powder Taimicron TM-DAR (Taimei Chemicals Co.,Ltd., 99.995% purity) with surface area of 13.7 m^2/g and primary particle size of 150 nm. Prior to the treatment, a small amount (approximately 1 g) of alumina powder was poured through a sieve on the surface of discharge ceramics (plasma area). The thin powder layer was covered with the shield glass plate. Alumina powder was treated in DCSBD operating in atmospheric pressure ambient air at input power of 400W for 1 minute.

2.3. Measurement

Luminescence experiments were performed on the photon-counting instrument Lumipol 3 manufactured by the Polymer Institute of Slovak Academy of Sciences, Bratislava, Slovakia. The measurements of glow curves (dependence of intensity on temperature) were done in a nitrogen flow of 25 mL/min. The weight of each sample was 80.0 ± 0.5 mg. The instrument dark count rate was 1–5 counts/s at 50 °C, spectral range of instrument was 290-630 nm.

3. RESULTS

The results shown in Figure 2 illustrate the compelling difference between plasma treated and non-treated alumina sub-micron powders at both qualitative and quantitative levels. Plasma treatment gave rise to two major peaks with maxima at 103 and 143 °C, while the non-treated sample exhibited only monotonic rise with the peak maximum located beyond the range of our measuring apparatus. The question at hand is: "What is the nature of the peaks created by plasma treatment - chemiluminesence or thermoluminescence?"

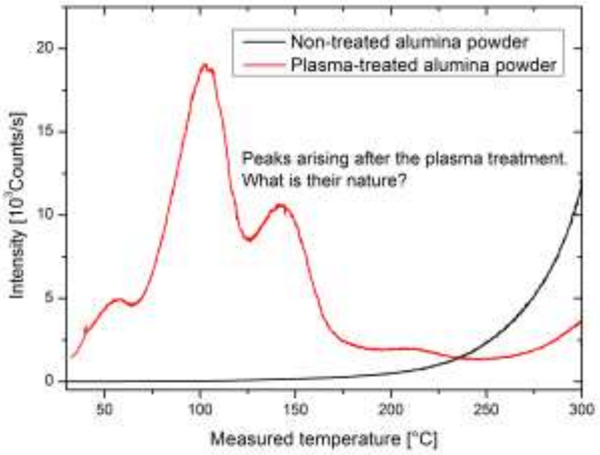


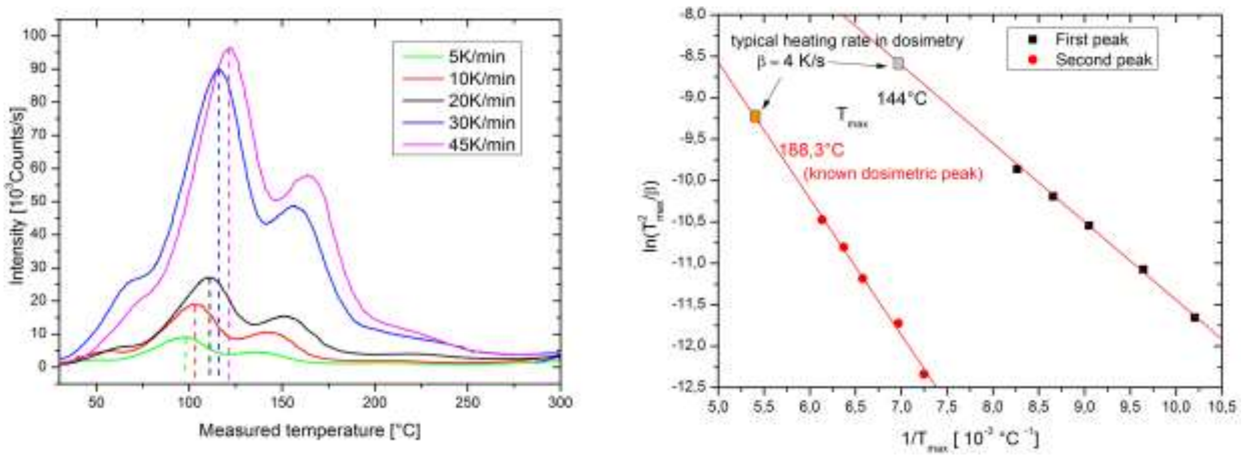
Figure 2 Difference between the glow curves of plasma treated and non-treated alumina sub-micron powder (β=10°C/min).

Theory of thermoluminescence (TL) gives the following relationship between the peak maxima and heating rates

$$ln\left(\frac{T_{max}^2}{\beta}\right) = \left(\frac{E}{k}\right)\frac{1}{T_{max}} + ln\left(\frac{E}{sk}\right), \qquad (1)$$

where T_{max} denotes temperature corresponding to the peak maximum, β heating rate, E trapping energy, k Boltzman constant and s the frequency factor [10].

We have therefore performed a set of luminescence measurements with various heating rates β to see the expected shift of peak maximum T_{max} when the heating rate is changed. Figure 3a shows that indeed T_{max} increases with increasing β. This corresponds well to typical observations of TL curves [11]. In order to verify the applicability of TL model on Figure 3a data, we plotted the left hand side of Eq. 1 (relationship between T_{max} and β) as a function of $1/T_{max}$. The resulting set of points shown in Figure 3b exhibits the predicted linear dependence. Therefore the trapping energy E could be determined from the plot slope (Table 1). The comparison of our data with the results of other authors has to be carried out with caution, since most of the reported TL glow curves are measured at high heating rates of 2 or 4°C/s. However the highest heating rate achievable by Lumipol 3 (device used in this work) was only 45°C/min (0.75°C/s). In Figure 2b we have therefore extrapolated our linear fit to the regions of heating rates up to 7.5°C/s. For heating rate of 4°C/s the measured T_{max} would be 144°C (first peak) and 188.3°C (second peak). The position of the second peak is in good agreement with TL study of Al_2O_3:C, where the peak maximum was located at 190°C [12,13].



a

b

Figure 3 (a) Glow curves of plasma treated alumina sub-micron powder for various heating rates; (b) Linear dependence verifying the consistency with TL theory (i.e. Eq. 1).

Peak position	T_{max} [°C]		Trap energy
	β = 10°C/min	β = 4°C/s	***E* [eV]**
1st peak	104	144*	0.08
2nd peak	144	188*	0.14

Table 1 Peak positions and their calculated trap energy. (* extrapolated data).

If the chemiluminescence (CL) is responsible for the detected emission, the ongoing surface chemical reactions should be sensitive to the change of working gas composition during luminescence measurements. In order to test this hypothesis, we measured the glow curves in N_2 and O_2 gas flows. Figure 4 clearly shows that, as far as the position of two main peaks are concerned, no significant change resulted from the change of working gas.

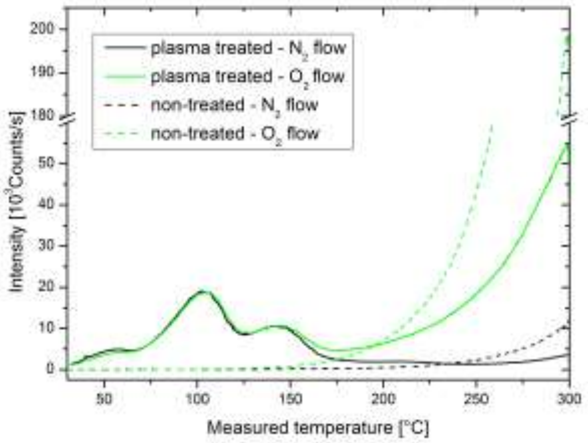


Figure 4 Dependence of glow curves on the working gas (β=10 °C/min).

4. CONCLUSION

Thermal stimulation of alumina sub-micron powder in range 30-300°C results in emission of light detected by photomultiplier detector. Plasma pre-treatment of alumina sub-micron powder causes a substantial increase of detected emission signal. Furthermore, the glow curve of treated alumina sub-micron powder exhibits a completely different shape to untreated powder. Two distinct peaks appeared in the region of 104 and 144°C. Our further experiments attributed these plasma induced peaks to the thermoluminescence effect, i.e. to an increase of electrons trapped in excited states of alumina powders. The existence of such electrons cannot be directly detected by standard surface diagnostics methods. Their role and importance for the processes of powders sintering or ceramic processing in general is still an open question.

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