Investigation of plasma treated alumina powders by chemiluminescence

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Chemiluminescence of dielectric barrier discharge treated alumina powders could be used with advantage as an effective diagnostic method for determining the efficiency and aging of plasma treatment. However the deflection of detected signal from theoretical prediction suggests that other radiation mechanisms are participating on overall luminescence signal. Presented series of complementary experiments confirmed, that indeed chemiluminescence is the main process behind the observed light emission. Further radiation process associated with plasma treatment was identified as recombination-induced luminescence.

1. Introduction

Chemiluminescence accompanies certain types of exothermic chemical reactions, usually of oxidative nature. It is commonly used for the detection of traces of hydrogen peroxide [1] and monitoring the oxidation stability of polymers [2,3,4]. 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. This is presumably emitted from the substrate due to the oxidation processes involving the hydroperoxides decay [5,6]. However the measured isothermal luminescence curves do not fully agree with the proposed model in the whole range. The discrepancy is most pronounced in the decay phase, after the peak luminescene intensity has been reached [2,7]. The observation suggests that another process or even more processes are involved. Two additional processes besides CL are described in [8] for the luminescence of plasma treated polypropylene at ambient temperature: UV excitation of chromophores and a long lived recombination-induced luminescence (RIL). In good agreements with this, authors of [9] claim for the luminescence of epoxies at liquid nitrogen temperatures, that the light detected at later times of experiment is emitted by the process of recombination. Thermoluminescence (TL) caused by thermal detrapping of electrons accompanied by emission of light can also play an important role at sufficiently high temperatures. The TL phenomenon is frequently employed in dosimetric applications [10,11]. Therefore, if only the spectrally unresolved signal can be obtained, one has to be very careful in interpreting the results and the relative participation of CL, RIL or TL.

In our experiments we investigated the luminescence of sub-micron alumina powder treated in low-temperature coplanar dielectric barrier discharge [12]. The process of chemiluminescence associated with the presence of hydroperoxides on the powder surface was intended to be used as an indicator of the plasma treatment. A method capable of rapid assessment of plasma treatment for powders was sought, since the conventional methods based on sessile drop measurements are not well suited for particulate materials, and capillary rise Washburn method [13], requires at least several grams of powder for a single measurement. This can be a major drawback when dealing with expensive powders, or when plasma treats at very slow rate due to its limited size or extremely large surface area of powders. On the other hand only tens of miligrams of powder are needed for the measurement of chemiluminescence. However as stated above the detected luminescence signal may comprise emission by other radiative processes besides CL. This paper presents our attempt to resolve the individual luminescence processes introduced to powder surface by dielectric barrier discharge plasma treatment.

2. Experimental

2.1. Plasma source

DCSBD (Diffuse Coplanar Surface Barrier Discharge) non-thermal plasma generator (Fig. 1) was used. It consisted of a screen-printed array of coplanar strip-like electrodes on the bottom side of a 96% purity Al_2O_3 plate with the thickness of 0.6 mm. 1.5 mm wide electrodes were separated by 1 mm gaps. 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 ceramic plate [12].

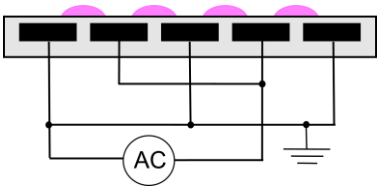

Figure 1 - Schematics of DCSBD setup. Only a reduced number of electrodes is shown for the sake of clarity.

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 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 instument was 290-630 nm.

3. Results

The shape of luminescence curve on Figure 2 clearly shows that indeed multiple processes are involved. Before the maximum is reached a shoulder appears, the origin of which had to be identified.

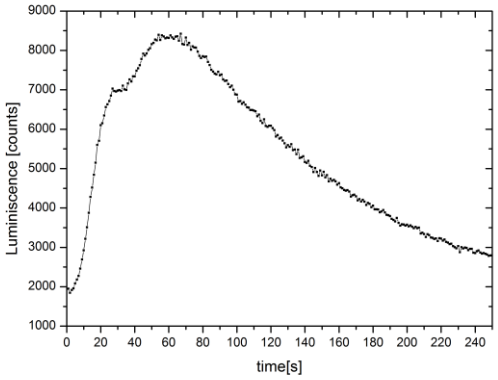

Figure 2 - Luminescence signal detected from plasma treated alumina powder (thermally cleaned at 600°C for 1 hour) in isothermal mode at 50°C.

Plasma treated alumina powders were left to age for a certain amount of time at ambient air, before investigated by chemiluminometer set to 120°C isothermal mode. The resulting curves are shown on Figure 3. It can be seen that as the peroxides (introduced to the surface by plasma treatment) decay during the aging process, the maximum of the curve decreases as well. Hence the dominant process present during the maximum can be assigned to the chemiluminescence, which is in good agreement with [8]. One can see, however, that even after 29 hours since plasma treatment, the effect of surface activation is still present.

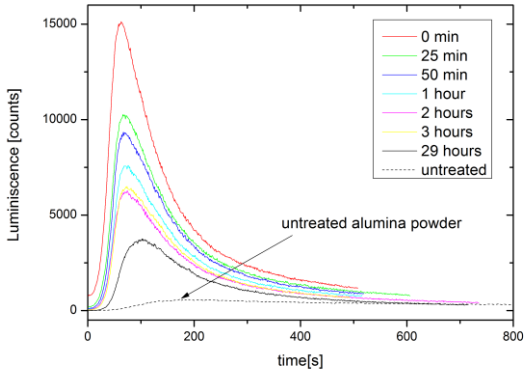

Figure 3 - Luminescence signal detected from plasma treated alumina powder in isothermal mode at 120°C for aging times 0 - 29 hours.

The more challenging part was to determine the process responsible for the shoulder appearance, which is most probably the same process responsible for the slower rate of luminescence decay. For this purpose we have performed a set of non-isothermal measurements for four distinct heat rates (2.5, 5, 10 and 20 °C/min). The resulting

curves on Figure 4 exhibit maxima at different temperatures.

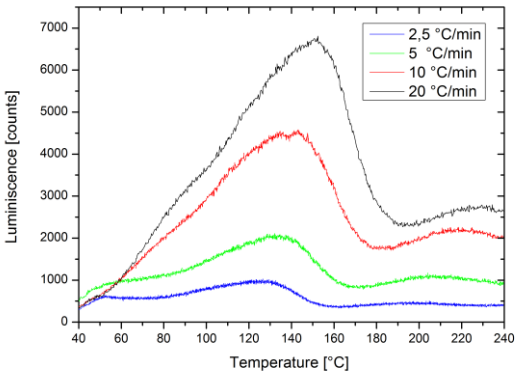

Figure. 4 - Luminescence signal detected from plasma treated alumina powder in non-isothermal mode for various rates of heating.

If the thermoluminescence was responsible, the maxima of the curves would be inherently independent of the rate of heating. According to the TL theory, the critical temperature depends only on the height of energy trap. In addition to that the minimum trap activation temperature reported for alumina TL is 390K [14]. In our case the luminescence signal was detected already at ambient temperature. These facts lead us to conclusion, that the process of TL can be excluded. The secondary process of light emission should be attributed to recombination-induced luminescence (RIL).

4. Conclusion

Luminescence measurements were performed on alumina powders treated by DCSBD. From the set of performed experiments it follows that the main processes contributing to the overall luminescence is the chemiluminescence, whereas the recombination induced luminescence starts to dominate in the later phases of the measurements. Participation of the thermoluminescence was excluded on the basis of non-isothermal experiments using various heating rates.

6. Acknowledgement

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7. References

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