

Control of Solid Surface Properties by Electron Beam Processing

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ABSTRACT

Electron beam modification of various solids (oxides, sulfides, ceramics, polymers) is shown to provide a control over their surface properties from the content of certain atoms and functional groups to overall hydrophilicity and reactivity depending on the process parameters. Particularly, the content of hydroxyl groups on the surface can be adjusted by the appropriate absorbed dose selection promoting either hemisorption of physically adsorbed water molecules or dehydroxylation and dehydration. The developed approach is successfully applied to enhance the exploration performances of such materials as fused silica useful for chromatographic capillaries, constructive ceramics, adsorbents, electroluminescent phosphors, polymeric substrates and coatings due to the improved compatibility between the irradiated components of these compounds.

Keywords: electron beam, absorbed dose, surface functional groups, modification, compatibilization

1 Introduction

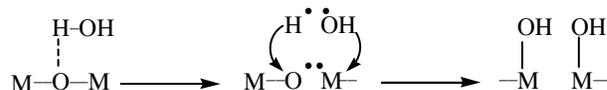
Electron beam processing is a promising approach to the control over the surface properties of various solids. The main advantages of electron beam technologies over the conventional chemical methods for surface pretreatment include the direct impact onto chemical bonds in the surface layer, possibility for the activation and control of adsorption-desorption processes, precise adjustment of the process parameters and absence of any chemical or radioactive contamination.

The effect of electron beam treatment upon various materials (oxides, sulfides, ceramics, polymers) is studied to clarify the general features of chemical reactions involving surface functional groups in correlation with the process parameters. The irradiation was carried out using a resonance transforming electron accelerator RTE-1V produced by the Efremov Institute of Electrophysical Apparatus (St-Petersburg, Russia) with the beam energy 500-900 keV and absorbed dose 50-500 kGy. The changes in the exposed surface properties were characterized by the adsorption of acid-base indicators with different pK_a values (distribution of Lewis and Brønsted sites according to their acidity strength), FTIR spectroscopy, contact wetting angle and surface tension measurements for boundaries with various liquids.

2 Results and discussion

2.1. Modification of oxides

Generally, electron beam processing of various oxides in air provides the control over the content of various hydroxyl groups and specific chemical bonds on their surface. For initially non- or weakly hydroxylated oxides (e.g. aerosils) irradiation at relatively small doses (50-100 kGy) leads to the dissociation of physically adsorbed water molecules into H^\bullet and OH^\bullet radicals interacting with the element-oxygen bridging groups to form hydroxyls [1]:



At higher absorbed doses (150-200 kGy) the surface of such materials undergoes dehydroxylation due to the disruption of relatively weak M-O-H bonds and overall dehydration.

In contrast, for some oxides featuring with initially hydroxylated surface (e.g. FeO, CuO) the lowest doses (about 50 kGy) promote dehydroxylation due to the disruption of weak O-H bonds in Brønsted acidic groups yielding oxygen bridges (Fig 1b). The further dose growth provides hydroxylation and dehydration processes according to the mechanism described above.

Oxides with higher cation charges such as Fe_2O_3 and Al_2O_3 also undergo dehydroxylation at low doses (~50 kGy) but acidic OH-groups are recovered at 200-300 kGy due to the presence of water molecules strongly bonded with Lewis acid sites and high metal-oxygen bond strengths requiring significant energies for disruption (Fig. 1c).

Upon the optimization of electron beam processing parameters the considered effects were successfully used for the following applications:

- modification of fillers for cements to impart them with enhanced strength performances and frost resistance due to the activation of solidification processes [2];
- pretreatment of oxide additives for ceramic materials providing up to 50% increase in their bent and compression strength due to the formation of additional hydroxyls at the surface promoting chemical binding of the particles through oxygen bridges upon annealing [1].

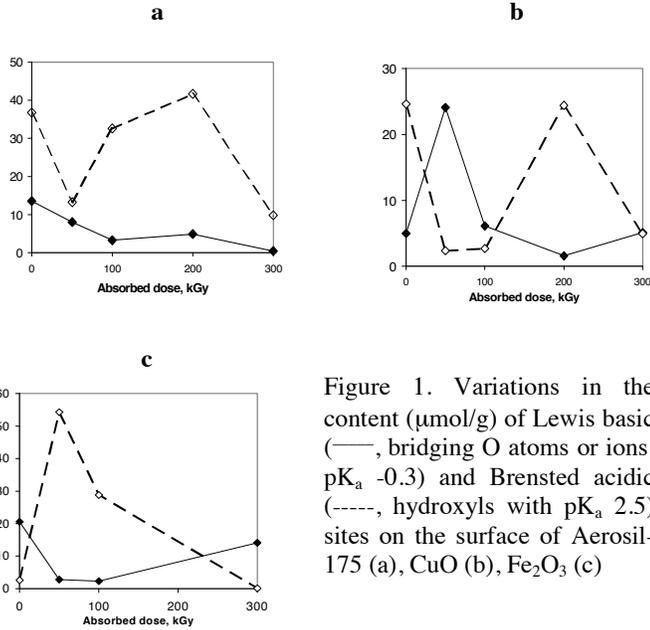


Figure 1. Variations in the content ($\mu\text{mol/g}$) of Lewis basic (—, bridging O atoms or ions, $pK_a \approx -0.3$) and Brønsted acidic (----, hydroxyls with $pK_a \approx 2.5$) sites on the surface of Aerosil-175 (a), CuO (b), Fe_2O_3 (c)

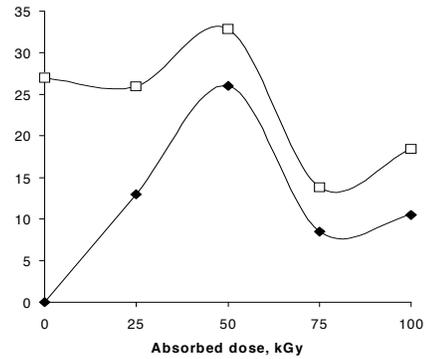


Figure 2. Effect of absorbed dose at electron beam (700 keV) pretreatment of fused silica glass on the content of acidic Brønsted centers (hydroxyls) with $pK_a \approx 2.5$ ($\mu\text{mol/cm}^2$) on the surface of fused silica glass samples after electron beam processing and efficiency of methacryloxypropyl-trimethoxysilane grafting characterized by the optical density ($D \cdot 10^3$) of the specific absorption band 2954.7 cm^{-1} (◆)

2.2. Functionalization of fused silica

Electron beam pretreatment of fused silica glass used for the production of chromatographic capillaries allowed a controllable functionalization of the glass surface. Particularly, the content of Brønsted acidic centers (silanol groups) on the irradiated fused silica surface is found to follow an “oscillatory” trend as a function of the absorbed dose below 100 kGy at electron beam processing due to the alternating reactions of hydroxylation (probably as a result of Si-O-Si bond disruption and interaction with radiolyzed physically adsorbed water) and thermal dehydration/dehydroxylation at radiation heating. The highest content of acidic hydroxyls with $pK_a \approx 2.5$ (measured using the adsorption of the acid-base indicator *o*-nitroaniline with the corresponding pK_a value) achieved upon electron beam processing with the energy 700 keV and absorbed dose 50 kGy provides the best conditions for the subsequent immobilization of methacryloxypropyl-trimethoxysilane (MOPTMS) layer as confirmed by the highest intensity of the absorption band at 2954.7 cm^{-1} intrinsic to stretching vibrations of CH-groups according to FTIR spectroscopy data (Fig. 2).

This approach allows imparting the initial fused silica glass surface with a stable, uniform and reproducible chemical functionality. Electron beam initiated grafting of MOPTMS provides the enhancement of the processes for the production of fused silica glass capillaries for electrochromatography and electrophoresis at the stage of an intermediate bifunctional layer formation required for the subsequent deposition of specific polymer coatings [3].

2.3. Enhancement of adsorbents

The controllable formation of specific functional groups on the surface upon electron beam processing is useful for the modification of their selective adsorption properties towards various compounds.

Electron beam treatment of natural sand taken from St-Petersburg suburban area Lahta (Russia) imparted it with adsorption activity towards Mn^{2+} ions growing with the increase of absorbed dose up to the saturation at 200–500 kGy (Fig. 3) due to the formation of Brønsted acidic and basic hydroxyls as well as Lewis basic sites.

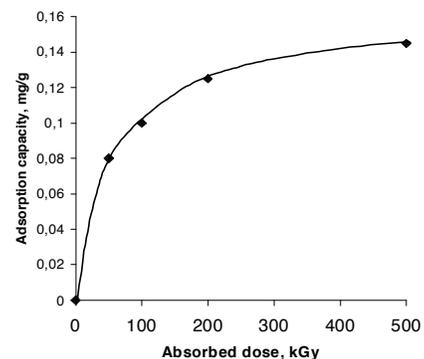


Figure 3. Adsorption capacity of sand towards Mn cations as function of the absorbed dose at electron beam pretreatment with the energy 700 keV

In another experiment commercial charcoal Dratnasirs 50-325 (produced from coconuts) with the average particle size 20 μm , specific surface 1150 m^2/g was irradiated at 700 keV and tested on the adsorption of Cu^{2+} ions as a model heavy metal pollutant in water. A certain increase of adsorption capacity was observed at a relatively low absorbed dose 50 kGy followed by a drastic decrease at higher doses (Fig. 4). The adsorption capacity was found to correlate with the content of Lewis basic and Brønsted acidic centers capable of binding Cu^{2+} ions according to the donor-acceptor and cation exchange mechanisms correspondingly.

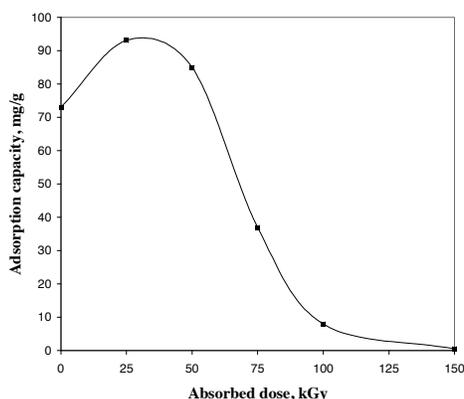


Figure 4. Adsorption capacity of charcoal as function of the absorbed dose at electron beam pretreatment

2.4. Enhancement of electroluminescent phosphors

Electron-beam processing of ZnS:Cu based electroluminescent phosphors (containing the optimal content of Cu doping additive about 0.3% wt.) provided a significant increase of their brightness, further improved upon an additional pretreatment of the initial charge mixture for their synthesis at a higher absorbed dose (Table 1). The observed effect is determined by the following factors:

- improvement of the doping additive diffusion into the material (particularly in the case of the initial charge mixture irradiation);
- decomposition of ZnS:Cu solid solutions;
- generation of specific defects promoting electroluminescent electron transitions;
- elimination of defects negatively affecting the electroluminescence. Particularly, adverse “electron traps” formed by sulfur vacancies and Lewis acidic (Zn, Cu ions) centers are shielded and “repaired” by electron beam processing at optimal parameters resulting in the disruption of Zn-S and Cu-S bonds and yielding of -SH and -OH groups according to the mechanism described above.

In addition, electron beam irradiation provides a certain stability enhancement for such phosphors and a possibility for the control over their emission spectra color due to the variation of the processing parameters.

Table 1. Relative changes in electroluminescence brightness of ZnS-Cu based phosphors prepared using 900 keV electron beam processing at different stages of the synthesis

Processing conditions	Electroluminescence brightness, %
Reference (no electron beam processing)	100
Phosphor synthesized from non-irradiated charge mixture and irradiated by electron beam at optimal absorbed dose 50 kGy	145
Phosphor synthesized from a charge mixture preliminarily irradiated at absorbed dose 500 kGy	160
Phosphor synthesized from a charge mixture preliminarily irradiated at absorbed dose 500 kGy and irradiated at 50 kGy after the synthesis	190

2.5. Modification of polymers

In our studies electron beam processing was successfully applied for the modification of the following polymeric materials:

- *Poly(ethylene terephthalate) (PET)* useful in numerous applications from supports for specific coatings and layers in various technical devices to bottles for beverages.

Electron beam processing of commercial PET films (45 and 100 μm thickness produced by AO “SVEMA” enterprise (Shostka, Ukraine) and Du Pont, USA) was performed with the energy 500 keV and absorbed dose in the range 25-500 kGy. The changes in PET properties were characterized by absorption of acid-base indicators, UV-vis and FTIR spectroscopy and contact angle measurements at boundaries with different liquids (water, isooctane, toluene).

Generally the analysis of surface sites distribution indicated that electron beam treatment of PET leads to surface reactions according to the mechanisms similar to those described above for oxides. The initial PET surface is predominantly occupied with Lewis basic centers with $\text{pK}_a -0.3$ (Fig. 5) formed by oxygen atoms in C=O containing ester groups. Processing at relatively low absorbed doses (up to 100 – 150 kGy) results in their transformation into hydroxyls ($\text{pK}_a 2.5$) [4].

The increase of absorbed dose to 200 – 300 kGy resulted in the opposite trend towards the surface dehydroxylation due to the removal of adsorbed water upon radiation heating.

