NANOTUBES INFLUENCE ON NANODIFFUSION OF HYDROGEN ATOMS AND ELECTRON TRANSPORT PROCESSES

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An investigation of carbon nanotubes (NT) influence on structural organization of matrix and electron transport processes is rather actual [1]. In present work it has been studied the influence of NT on the processes of low temperature (77K) radiolysis, injection and transport of electrons, their stabilization and acceptance by protons to form $H^\bullet$ atoms during irradiation of glassy matrix of sulfuric acid (H_2SO_4 98% + H_2O 2% mass.). The influence of NT individualized by ultrasound on the processes of $H^\bullet$ nanodiffusion at their decay is explored also. ESR method has been used to study both the kinetics of paramagnetic centers accumulation during the radiolysis and the processes of their decay at heating of irradiated samples.

The main mechanism of strong mineral acid radiolysis at low temperatures consists in elimination of an electron from an anion of acid remainder. Then in its injection and transport in to ambient matrix, slowing down (including subsequent acts of inelastic scattering and/or secondary ionization), thermolysis, and capture by a proton to form $H^\bullet$ atom. In Fig.1a the ESR spectra of irradiated samples of H_2SO_4 and H_2SO_4+NT are given. Characteristic doublet with a splitting ΔH=50,5 мT belongs to ESR spectrum of $H^\bullet$ atom. The middle part of spectrum is due to paramagnetic centers $R_S^\bullet$ formed during the radiolysis of anions of acid remains. ESR spectra of $H^\bullet$ atoms and «heavy» particles $R_S^\bullet$ are identical for pure H_2SO_4 and for H_2SO_4+NT, and direct «chemical» interaction between $H^\bullet$ + NT was not revealed. However, the presence of nanotubes practically doubles the accumulation rate both of $H^\bullet$ and of $R_S^\bullet$ radiation yields turned out to be $G_H(H_2SO_4) \cong 0.035$, $G_H(H_2SO_4+NT) \cong 0.07$; $G_{Rs}(H_2SO_4) \cong 1.1$, $G_{Rs}(H_2SO_4+NT) \cong 2.3$ 1/100 eV, respectively. An enhancement of radiation yields G_H and G_{Rs} in presence of NT evidences their influence on the radiolysis processes, energy transfer, and the process of charge transport in the matrix H_2SO_4+NT. Taking in consideration the concentration value of NT C_{NT} =0.16-0.36% mass one may conclude that this influence spreads on distance at least comparable with that one between NT and measured in 100-300 nm. Usually including of high conjugated adds «protect» the matrix from damage during the radiolysis and radiation chemical yields of matrix decay as well as radiation chemical yields of radicals decrease.

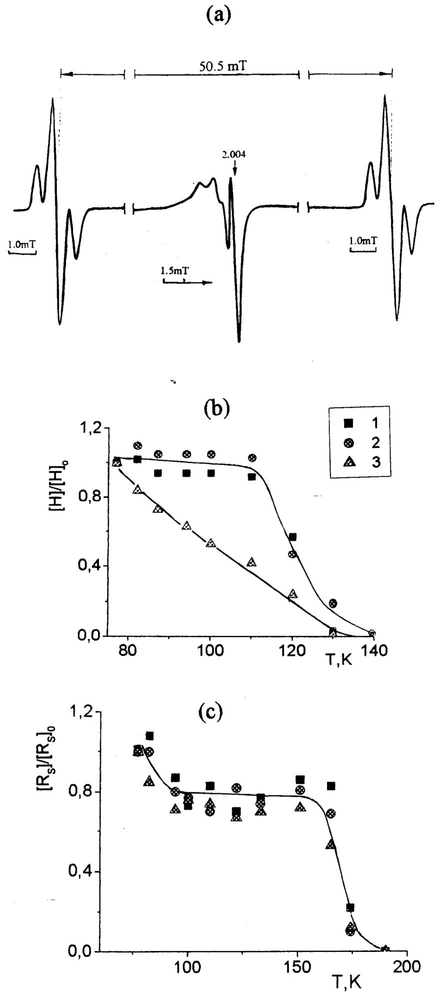

Fig.1. ESR spectrum of γ–irradiated (at 77 K) of 0,16% nanotube solution in sulfuric acid (a); temperature dependence of H-atom concentration (b) and R_S radicals (c) during the heating of irradiated solutions NT in sulfuric acid with concentration 0.38 (1), 0.16 % (2) and pure H_2SO_4 (3).

The observed simultaneous enhancement of G_H and G_{Rs} is connected apparently with additional injection of "quick" electrons from NT during the radiolysis. By so doing the probability of $H^\bullet$ atoms stabilization retains the same being about of $G_H / G_{Rs} \approx 0{,}032$.

In the processes of active radicals recombination and decay the stage of their nanodiffusion approaching is limiting. At the same time, if «bulky» molecular particles (such as $R_S^\bullet$) move accordingly to vacant mechanism so for the «small» $H^\bullet$–atom the mechanism of diffusion between bundles is available [2]. In Fig.1 b and c the curves of thermal decay of $H^\bullet$ и $R_S^\bullet$ during stage by stage heating of γ-irradiated samples are given. As seen, the form of curves of $R_S^\bullet$ decay does not depend on NT presence and an efficient recombination takes place near the matrix devitrification temperature $T_g \approx 175K$. The decay of $H^\bullet$ takes place at lower temperatures (what is in a good agreement with the between bundles mechanism of $H^\bullet$diffusion), the presence of NT sharply narrowed the interval of an effective recombination. A wide temperature interval of $H^\bullet$ decay in pure H_2SO_4 reflects the kinetic inequality of the process caused by the dispersion of activation barriers and of traps depth. [3]. Thus, the NT presence mainly influences on nanodiffusion processes between bundles decreasing their kinetic inequality and improving physics heterogeneity of solid vitrificated matrix surrounding the NT. Rather possible that NT presence to significant extent relieves the mechanical tensions created during "annealing". This fact can turn out to be a very important at the creation of different composed materials. At that, as well as in the case of electron transport during the radiolysis NT influence extends rather far away for 100 – 300 nм and even more. It should be noted that in [1] extend "organized" NT influences on the crystallization processes of pure sulfuric acid (H_2SO_4 100% + SO_3 2%) have also been revealed.

References

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