Dynamical forming and applications of nanocomposites from organic and inorganic components for new trends in material research and technologies

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Abstract. The composite scintillators from inorganic scintillators and organic phosphors provide unique combination of high light yield and nanosecond temporal resolution. Preparation of microfibers of these composites by means of centrifugation resulted in forming of axial nanosplitting and transverse micromodulation of their structure and optical properties. These modulations result in essential improvement of scintillation parameters of the composite providing the development of relatively simple and cheap X-Ray microscope. Ball rolling of inorganic solids provides superfast introduction of organic and inorganic components into subsurface layers for the special modifications of their properties. The superfast introduction is explained by propagation of nanocracks involving necessary dopants into the solid.

1. Introduction
Studies on forming of nanostructural and nanodimensional solids became highly actual during the last 30 years due to a wide set of profitable advantages of their properties [1-5]. On the other hand composites from organic and inorganic microdimensional components are applied as constructional and electrical materials for rather a long period of time [6-10]. So the developments and investigations of the composites with nanodimensional organic and inorganic components have promising prospects either for getting good knowledge about the nature of materials or for creation of more effective applications. Development of new scintillators from organic phosphors impregnated with inorganic nanoparticles providing record characteristics of a new kind of radiation detectors [12-14] confirms wide prospects of combining of organic and inorganic nanocomponents [15-17]. This paper is dedicated to several new trends of these activities.

2. Methods of experiments
We found that preparation of microfibers from the composites of polystyrene phosphors activated with PPO and inorganic scintillating nanoparticles of cesium sulphate activated with thallium reveal a set of new structural particularities of this composite followed with several essential improvements of radiation detectors based on these materials. These fibers were prepared from solutions of activated polystyrene in toluene impregnated with nanoparticles of cesium sulphate...
activated with 0.1% of thallium. The preparation was made in two ways. In the first case the solution of the composite was poured onto a disk of a centrifuge installation. Then the rotation of the disk was switched on with angular velocities from 20 to 30 rotations per second. Video registration of the processes taking place during the rotation with temporal resolution of 0.02 sec revealed forming of liquid drops at the edge of the disk followed by transformation of theses drops to long microfibers pushed out from the disk. The diameters of the fibers varied from 1 mcm to 50 mcm depending on the dimensions of the initial drops and the frequency of the rotations. When 0.5x1 cm walls were installed along the external circle of the disk with the interval 1 cm between them many fibers turned out to be fixed between these walls. The systems of these fibers had the form of parallel to each other straight lines (Fig.1) with much better homogeneity of the diameters.

![Figure 1. Optical polarization microscopy of the composite fibers formed by centrifugation between the walls at the disk edge. The horizontal dimension of the photo is 300 mcm](image)

Another technique used pulling of single fibers out of the solution by means of a glass stick touching initially the surface of the solution. The diameter of the fiber was decreasing gradually during pulling. At the beginning the fiber had the circular cross-section. Then after some thinning the form of the cross-section became dumbbell-like. In this case screw-like or sinusoidal-like geometries of the fiber were observed (Fig.2). After further thinning the fiber became cylindrical again.

Studies of morphology of these fibers by means of optical and scanning electron microscopy revealed two kinds of structural modulation. The first one is the transformation of the cylindrical continuous fiber to a bunch of thin threads parallel to the axis of the initial fiber. The second kind concerns the microscopic modulation of the lateral surface and the refractive index of the fiber (Fig. 3, 4).

This modulation includes scales from mesoscopic (several tens of micrometer) to nanoscopic (several hundreds of nanometers). The longitudinal splitting to parallel threads can be attributed to instabilities of the lateral surface of the initial fiber to the curvature fluctuations connected with non-homogeneity of evaporation of the solvent induced with the curvature. If a semi-cylindrical protuberance appears at the surface the speed of the evaporation is increased locally inducing accelerated solidification. The volume of the solution inside this protuberance will
Figure 2. Sinusoidal (left) and screw (right) forms of the composite fibers pulled out from the colloidal solution of polystyrene and cesium sulfate nanoparticles in toluene.

Figure 3. Electron (left) and optical (right) microscopies of the axial splitting of the fibers.

Figure 4. Optical polarization microscopy of the composite microfiber demonstrating the periodical modulation of its optical properties. The length of the photograph is 200 mcm.

decrease resulting in soaking of the substance from other internal regions. The soaking processes will provide the splitting of the internal continuous substance to a set of threads. The creation
of dumbbell-like fibers as well as their transformations to screw and sinusoid geometries can be attributed to instabilities of the rate of evaporation connected with the surface curvature. Elliptical perturbation of the circular cross-section induces increase of evaporation in the regions of increased curvature and subsequent increase of solidification. Accelerated solidification induces soaking of the liquid substance from neighbour regions with corresponding creation of the dumbbell-like geometry. Accelerated solidification of one side with corresponding shortening of its length will induce compression of the opposite side and its bending. This asymmetrical bending will result in screw and sinusoid distortions of the geometry.

The modulation of the geometry of the lateral surface and of the refractive index along the fiber can be attributed to well-known Rayleigh-Tailor instabilities connected with variations of surface tension due to changes in local diameter of the fiber [18]. Fluctuation decrease of the diameter induces increase of local Laplace’s pressure with corresponding redistribution of nanoparticles filling the solution modifying the refractive index (Fig. 4).

The microscopic and nanoscopic modifications of geometry and optical parameters of the composite fibers are followed with essential variations of the parameters of their X-ray luminescence. Studies of spatial and polarization distributions of the luminescence from bunches of parallel fibers revealed significant anisotropies of these characteristics [19]. The light emission along the fibers was stronger than normally to them. And the intensity of the light in the polarization parallel to the fibers was about 3 times higher than the intensity perpendicular to them. These anisotropies are explained with the particularities of the morphology of the fibers described above. The periodical modulations of the refractive index and the lateral surfaces along the fibers arrange the distributed feedback for the emitted light. This feedback enhances the emission along the fibers [20]. The preferential parallel polarization of the emitted light is attributed to the waveguiding localization of the light propagation along submicron threads formed within the fibers [21, 22].

The enhancement and preferential localization of the light emission along the composite scintillation fibers formed by means of the dynamical procedures described above provide the development of comparatively simple X-Ray microscopes based on the matrices assembled from parallel scintillation fibers. These matrices will be capable to analyze the spatial distributions of the X-Ray flows with the resolution corresponding to the diameters of the fibers. The objects to be examined by the transmission or the reflection of the X-Rays can be illuminated with point-like or synchrotron sources of X-rays [23]. In the both cases the microscope will not need complicated and expensive X-Ray optics. For the point source the microscope will use the principle of camera obscura [24]. This principle will arrange magnification without additional optics determined by the ratio of the distance from the object to the detector matrix to the distance from the object to the point source. These X-Ray microscopes are needed in material research, biology, medicine, gamma-telescoping, etc. In addition to microscopical spatial resolution the scintillation composite microfibers provide essential improvement of the sensitivity due to the increase of the amount of the emitted light photons and decrease of the light emission time. So the intensities of X-Ray irradiation of objects under micro-examination in this case can be decreased by several times with respect to usual detectors. This improvement decreasing the irradiation doses is important especially for in situ observations of living biological objects.

The results presented above concern advantages of organic-inorganic composites when inorganic nano-inclusions are introduced into organic matrices. Naturally it would be interesting to study the situation vice versa when organic molecules or their agglomerations are introduced into inorganic matrices. But usually introduction of any inclusions into inorganic solids is carried out at elevated temperatures when organic substances are destroyed. We have developed a new technique for introduction of various foreign nano-inclusions into solid materials by means of ball rolling of the surface with a layer of the substances to be introduced. We found that at room
temperature the introduction of either organic or inorganic nano-inclusions into various solids (crystalline metals, dielectrics, semiconductors as well as amorphous glasses) by means of ball rolling proceeds faster by several orders of magnitude than introduction at temperatures about 1000°C by means of usual thermal diffusion [25]. For example Fig. 5 presents the transverse optical microscopy of the introduction of carbon nano-particles from water suspension placed on the surface of cesium iodide single crystal by means of the ball rolling. After 5 minutes of rolling the depth of the introduction of carbon nano-particles achieved fifty micrometers. Cesium iodide is used here as an optically transparent material with the mechanical properties close to the properties of plastic metals (copper, aluminum, etc.) as a model of their behavior during the ball rolling.

Figure 5. Optical microscopy of the superfast introduction of the carbon nanoparticles into the cesium iodide single crystal by the ball rolling. The length of the photograph is 200 mcm.

Besides we observed experimentally that organic polymers are introduced into inorganic crystals rather quickly as well. For example polymers of teflon (polytetrafluoroethylene “PTFE”) in the form of submicron particles (0.2 - 0.3 mcm dimensions) have been introduced into steel plate by means of ball rolling. The particles of teflon were placed initially onto the surface of the plate in the form of aqueous suspension. Then the plate was subjected to the rolling by a hard steel ball with 4 mm diameter during 5 minutes. The remnant suspension was removed from the surface after the rolling by means of frictional cleaning with a piece of cotton fabric and liquid acetone. Then drops of water were placed at two regions of the steel surface: initial and subjected to the rolling with teflon (Fig. 6).

The difference in the forms of the drops demonstrates clearly that the initial part is wetted rather well whereas the rolled region is not wetted. Hence the Teflon particles have been inserted into the subsurface deeply enough and were not removed with the acetone frictional cleaning providing its hydrophobic behavior of the plate.

Scanning electron microscopy studies of the surfaces of steel samples as well as of other metals subjected to the ball rolling reveal creation of quazi-periodical system of straight lines parallel to the direction of the rolling crossed by submicron cracks and other breaks of continuity (Fig. 7, 8).
Figure 6. The drops of water deposited onto the surface regions of the steel sample: the left one was not rolled. The right region was subjected to the ball rolling with the suspension of the teflon nanoparticles.

Figure 7. Electron microscopy of the surface of aluminum subjected to the ball rolling with the close to periodical systems of straight lines parallel to the direction of rolling.

The edge of one of bigger breaks going normally to the surface of the aluminum sample after rolling (Fig. 9) revealed quasi-periodical nanostructure of layers parallel to the surface.

These rather complicated structures of subsurface regions of crystals after rolling lead to the assumption that these complications appeared due to highly inhomogeneous pattern of internal stresses changing periodically their signs and directions in any point of this region during the rolling process. For example micro- and nano-cracks being opened and closed periodically in correspondence with the reciprocating motion of the rolling ball provide rather fast penetration of nano-components of foreign substances from the surface towards the depth. The local expansion stress in a certain moment opens a nano-crack starting from the surface. Due to the decrease of the stress the crack interrupts its propagation from the surface at a certain depth. Several
Figure 8. Electron microscopy of the steel surface subjected to the ball rolling. The lines parallel to the direction of the rolling are crossed with perpendicular nanocracks (at the left)

Figure 9. Electron microscopy of break in the surface of aluminum sample subjected to the rolling revealing the periodical system of nanolayers parallel to the surface

foreign nano-components from the suspension placed to the surface earlier are attracted inside the crack. When the direction of the motion of the ball is reversed the sign of the stress at the cracks is changed as well and the compression produced by the ball at this moment acts for the closure of the crack. But the edges of the crack trying to approach each other meet the nano-particle placed inside the crack and working as the obstacle for the closer. Due to the lever rule the stress acting at the surface on the crack edges at its spike is multiplied by a ratio of the distances from the surface to the nano-obstacle to the distance from this obstacle to the tip of the crack. If a crack has simple triangle geometry this value is determined by the ratio of the upper width of the crack to the diameter of the nanoparticle. When the nanoparticle inside the crack is close to its tip, this lever multiplication can exceed 10 times or more. Hence the local compressive stress is transferred from the surface to the depth of the sample by joint actions of nano-cracks and nano-particles. At the tip of the crack the compression is reversed to the
enhanced tensile stress which can achieve the value capable to induce further propagation of the crack towards the depth. At the moment of the tensile stress at the surface side of the crack it will attract additional portion of nanoparticles and the process of unusually fast transfer of the foreign material towards the depth of the subsurface region will be prolonged during the next change of the sign of the stress.

Parallel lines at the surface formed during ball rolling along the reciprocating trajectory of the ball as well as big amount of spherical nanoparticles of the material subjected to rolling in the vicinity of the trajectory can be explained by active participation of these nano-spheres in the mass transfer during the rolling. So in addition to the well known mechanism of generation and motion of dislocations, as well as described above creation and propagation of self-consistent system of sign-alternating stresses, nanocracks and nano-particles one more version of the mass transfer can work during the rolling based on longitudinal motion of nanograins. The yield of each of these processes depends on the details of the rolling procedure and characteristics of the material being rolled.

The mechanisms of self-consistent propagation of nanocracks and nano-inclusions seems to be the most effective for the accelerated transfer of foreign substances into the subsurface regions of solids by means of the surface ball rolling. Many different substances can be introduced by this way (either organic or inorganic). For a wide set of technical applications the subsurface layers of solids determine their exploitation parameters in mechanical constructions, electronic and optical devices, biomedical instruments, etc. Anticorrosion and antifriction protection of metal construction elements, subsurface doping of insulators for optical waveguides or semiconductors for electronics, introduction of biopolymer molecules like proteins, DNA, etc. for biosensors and many other prospective applications can be developed using the results of this paper. It should be emphasized that introduction of organic polymers (either biological or synthetic) into matrices from metals, semiconductors or dielectrics produces qualitatively new materials promising generation of many unusual properties. For example the transverse characteristic dimensions either of dislocations in inorganic crystals or of synthetic and biological polymers are comparable [26]. So introduction of polymer molecules into inorganic crystals can create qualitatively new nanostructure: states of dislocations and polymers bound mutually demonstrating unexpected kind of behavior in mechanical, electronic, optical and other properties. The preparation of these composites was problematic earlier because usual introduction of foreign substances into solids requires elevated temperatures when organic molecules are destroyed.

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