Self-concentrated mass-transfer during deformation treatments of organic-inorganic compositions

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Abstract. This paper prolongs the series of our previous papers where we found super-fast and super-deep introduction of foreign substances in crystalline materials by means of the ball rolling. A set of new experimental results was used to justify the new version of the mechanism of this introduction with the record speed and depth. The main process which determines this phenomena is connected with the sequence of openings and closings of nanocracks at the surface subjected to the rolling and the capture of the substance introduced from the surface by these cracks. The process of this introduction with the record parameters is supported by the intense chemical interactions between the matrix and the substance being introduced. This chemical interaction is intensified by several times with the deformation treatments. The analogous super-fast mass transfer is observed in the situation of the pulling out of the polystyrene fibers from the solution of polystyrene in benzene when the interaction of the organic components with cesium iodide nanoparticles was activated by the deformation treatment of the solution during its pulling out resulting in the formation of big amounts of nano-channels promising for effective utilization of hazardous radioactive wastes.

1. Introduction
This paper is a prolongation of our works on the scintillating radiation detectors and other profitable useful compositions of inorganic and organic raw materials [1-4]. R&D studies on various compositions from organics and inorganics are developing rather quickly resulting in new materials for electronics, nano-optics, biomedicine with sufficiently improved properties [5, 6]. Our works on the composite scintillators confirm the productivity of assembling in the unified material of the advantages of organics (fast light emission and high light yield) with high stopping power and good radiation hardness of inorganics achieving the scintillating material with record combination of the technical properties and the low-cost and convenient production technology [7, 8]. One of the main characteristics of the composite scintillators is the atomic-electron structure of the bonds between the organic and inorganic constituents. This structure determines the quality of the transfers of the electron excitations and atomic-molecular vibrations between the components which are responsible for the whole set of the scintillation parameters of the material. Our former papers [1-4] and another our paper of this issue are devoted to the studies of the formation, infrared and visible optical spectra of the composites which delivered the useful information about the behavior of the bonds organic-inorganic in various conditions. Rare earth fluorides and cesium sulfate were used as inorganic fillers whereas the activated polystyrene phosphor was applied as the binding matrix of the composites. In this paper we changed the inorganic filler and took cesium iodide crystals instead of the fluorides and cesium sulfate. The
choice of cesium iodide is justified by three reasons. This material is well known for specialists in nuclear physics and nuclear energy because on the one hand CsI crystals are the most common material for radiation detectors and their interaction with ionizing radiation has been studied in details [7]. On the other hand, radioactive cesium and iodine belong to the most common waste materials of nuclear fission. So their utilization by means of the interactions of these substances with various organic and inorganic materials have been studied during many years [9–14]. The active interactions of cesium iodide and its components with organic materials belong to one the promising results of these studies for the applications of cesium iodide in the compositions for the studies in this paper. [12-14]. For example, cesium is capable to create strong bonds with the carbon atoms of the benzene rings or phenyl groups, whereas iodine forms complexes with the same rings and is capable to form bound states with hydrogen. So it is natural to expect any signs of these interactions in the compositions of cesium iodide with polystyrene and benzene. And several manifestations of these interactions have been found here indeed.

We used two techniques of preparation of these compositions which are quite different from each other [3, 4]. The first one used introduction of any foreign substance into the sample of solid cesium iodide by means of the ball rolling of the upper surface of the crystal with this foreign substance deposited onto the surface. As the second method we used the solidification of the solutions of polystyrene in benzene with various contents of cesium iodide in the forms of micro- or nano-particles inserted into the solution. The solidification was made by means of pulling of a jet of the solution with a thin glass stick touching the surface of the solution before the pulling. The speed of the pulling out was regulated from 0.5 cm/sec to 20 cm/sec. In spite of the severe differences in the methods of the preparation of the composites several analogies in the structures and properties of these compositions have been found. They are described below.

2. The results of the experiments and their discussion

In the previous paper [4] we paid attention to two types of unusual geometries of the trajectories of the polystyrene molecules introduced into single crystalline cesium iodide by means of the ball rolling: the dagger-like regions going preferentially in perpendicular to the surface subjected to the rolling and thin and long filaments oriented analogously. The formation of the “daggers” could be attributed to the creation of a new kind of a mixed material from cesium iodide and polystyrene appeared due to the active interaction between these substances stimulated by the intense deformation treatment. The ‘dagger’ formed by this way could be harder significantly with respect to cesium iodide. So the compressive stresses from the ball taking place at some positions of the ball were capable to drive this “dagger” as a nail into the crystal. In order to clarify this question, we studied the dynamics of the introduction of polystyrene by means of the optical microscopy. It turned out that the sharp apexes of these “daggers” did not create significant concentrations of the internal stresses which should be present in the case of the “driving in”. Moreover, the introduction of thin and long threads cannot be explained by the “driving in” process due to the fact that these threads are too flexible.

Detailed examination of the dynamics of the introduction of the polystyrene molecules as well as of the carbon particles induced the alternative assumption about the mechanism of the super-fast and super-deep introduction of foreign substances by the ball rolling. This process was registered by the polarization-optical microscope equipped with the video-recorder. The optical axis of the microscope during the observations was oriented along the surface subjected to the ball rolling and perpendicular to the direction of the introduction of polystyrene [4]. The spatial resolution of the optical microscopy varied from 2 to 10 micrometers by changing the objectives. Figs. 1 – 4 demonstrate the stages of introduction of polystyrene to cesium iodide. The optical microscopy photos at Fig. 1. show the initial stage of the rolling. The long dark threads with the thicknesses of several micrometers penetrated into the subsurface layer rather deeply (the depth of their penetration achieves 300 micrometers). It is seen clearly that the
Figure 1. The optical microscopy of the initial stage of the introduction of polystyrene molecules into cesium iodide by means of the ball rolling. The horizontal dimension of the region shown at the photo is 2 mm.

penetration is not connected with the “driving in” or “pressing in” of any hard daggers. One of the daggers is emerging at the right edge of the upper photo. At least 4 emerging daggers are seen at the next photo. The patterns of their formations lead to the assumption that these daggers result from the deep penetration of polystyrene in the forms of threads but not vice versa. Rather a wide variety of the geometries of these threads is observed. Some of them are oriented at the angle of 45° with respect to the surface, i.e. in the most profitable direction for the plastic deformation. Other straight threads are perpendicular to the surface. But on the other hand several threads look like rather curved arks. These observations make us to conclude that the geometry of these threads do not determine the directions of the mass transfer.

Three polarization-optical micro-photos of the morphologies of the subsurface layer of the cesium iodide crystal at the next stage of the introduction of polystyrene are presented at Fig. 2. The upper photo made in the transmitted light through the crossed polarizers shows several daggers formed by the rolling under the surface, placed at the upper part. It is worth to emphasize that no signs of the production of any internal stresses are seen at these photos. This is one more evidence that the “daggers’ were the results of the deformation mass-transfer but
they were not the actual participants of this process and were not pressed into the crystal.

The third photo presented at Fig. 2 shows the polarization - optical microscopy in the transmitted light of the region presented at the second photo but in the perpendicular direction. The third photo presents the appearance of the rolled cesium iodide crystal when the polarized light propagated in the direction parallel to the daggers shown at the middle photo. The bright spots in the middle part of this photo correspond to the points of the entrances of these daggers into the crystal. The brightness of these spots in the crossed polarizers manifests severe optical anisotropy of the internal structure of these daggers. This information is important for understanding of the mechanism of the formation of these daggers during the rolling of cesium iodide surface with polystyrene solution deposited onto the surface subjected to the rolling.

Our microscopical observations of the dynamics of the rolling processes of the cesium iodide crystals with polystyrene deposited preliminary onto their surface revealed that these “daggers” are created by accumulation of the thin threads produced by the rolling at its initial stages. The emerging of these accumulations were shown at Fig. 1. The micro-photo at Fig. 3 demonstrates this process of the emerging of the “daggers” more clearly. In these cases the molecules of polystyrene were introduced into cesium iodide by the ball rolling. All long enough threads at this photo demonstrate mutual attractions resulting in the formation of the initial stages of the “daggers” with the geometry of sharp apexes.

The information from publications about the active interactions between cesium and iodine with various organic substances including polymers and benzene was presented in the Introduction.

This information combined with the experimental facts described above made us to prepare the new version of the mechanism of the super-fast and super-deep introduction of organic substances into cesium iodide. The last photo (Fig. 2) of the surface of the cesium iodide sample subjected to the ball rolling besides the optical anisotropy demonstrates the traces of the micro-cracks produced by the motions of the ball. We suppose that these cracks are the main participants in the mass-transfer process. The scheme of this process is presented at Fig. 4.

The ball 1 is rolling back and forth along the surface of the solid sample with the substance deposited onto this surface (blue small balls). When the tensile stress induced by the ball in the subsurface layer stimulates the creation of the crack, some portion of the substance is inserted into the crack by the ball and by the natural attraction of this substance to the fresh surface of cesium iodide. The capability of the substance for the active interaction with the solid facilitates the fast penetration of the substance into the crack. The return movement of the ball tries to close the crack, but the compound formed by the surface substance with the walls of the crack create essential resistance against this process. Due to the rule of the lever the compressive stress created by the ball at the top of the crack is transformed to the tensile stress at its mouth. If the stress is sufficient the crack below the internal substance opens wider and the compressive stress pushes the introduced substance deeper. This version is capable to explain either superfast and super-deep introduction of foreign substances by the ball rolling or the formation of super-thin and super-long filaments of foreign substances inside the subsurface layers of solid subjected to the ball rolling. This means that the threads decorate the edges of the cracks when they do not move.

It is necessary to emphasize that the interactions between cesium iodide with polystyrene or carbon in ordinary conditions is not observed. But when the crystal is subjected to the deformation treatment the interaction is enhanced by many times. The reasons of this enhancement are connected with the modifications of electron states of cesium, iodine, polystyrene and carbon subjected to mechanical loads [16]. Detailed studies of the influence of the deformations on the electron states of these substances will be studied later.

Anyway the experiments described above manifest the ability of various combinations from
Figure 2. The optical microscopy of the subsurface layer with the “daggers” from polystyrene molecules introduced by the ball rolling (two upper photos). The third photo shows the transmission optical microscopy of the “daggers” introduced by the ball rolling showing that the daggers have optically anisotropic internal structures.
Figure 3. The optical microphoto of the super-long thin threads produced from polystyrene and introduced into cesium iodide by the ball rolling which demonstrates the start of the accumulation of the threads into “daggers”.

Figure 4. The scheme of the super-fast and super-long introduction of foreign substances into solids by means of the ball rolling of their surface with these substances deposited onto it.

cesium iodide and its constituents, polystyrene and carbon being subjected to some kinds of the deformation treatment to form new phases and new compounds. Hence these interactions turn out to be profitable from thermodynamics point of view, facilitating creation of various super-structures by means of self-organization [17, 18]. Some signs of these manifestations of the self-organization can be noticed at the Figures presented above. For example, the spatial distributions of the “daggers”, micro-threads and some other traces of the rolling introduction demonstrate signs of periodical or fractal super-structures. The quasi-periodical distributions of the micro-threads parallel to the directions of the dislocation glide bands of cesium iodide at the initial stage of the rolling and analogous quasi-periodical distributions of the “daggers” at the later stages result from usual competitions of the internal energy factors trying to place the
Figure 5. The transmission optical microscopy of the spatial distributions of the foreign substances introduced into the basic matrices: Top – polystyrene into cesium iodide matrix by means of the ball rolling. Bottom: cesium iodide particles into polystyrene matrix by means of pulling out the fibers from the solutions doped with inorganic particles interacting substances as close to each other as possible and the diffusion and entropy factors trying to disturb these signs of self-organization [17, 18].

In spite of significant differences between the processes of preparation of the compositions organic – inorganic by means of the ball rolling and by means of the pulling out the fibers from solutions some results obtained in these two kinds of the studies are close to each other. For example, the spatial distributions of the polystyrene molecules introduced into cesium iodide by rolling and of the cesium iodide micro-particles introduced into the polystyrene fibers by the preliminary introduction of these particles into the solution of polystyrene in benzene and subsequent pulling out the composite fibers resemble each other (Fig. 5).

The photos presented at Fig. 5 manifest the obvious likeliness in the distributions which are “vice-versa” mutually. In the both cases the degree of the periodicity is determined by the ordering attraction between cesium iodide and polystyrene components and disordering factors induced by thermal and diffusion processes. Concerning the fibers of polystyrene doped with cesium iodide particles the attracting interactions organic-inorganic between these two substances resulting in super-fast and super-deep introductions in the case of the ball rolling gave a new interesting structural feature in the case of the fibers. When the speed of pulling out of the fibers was low enough the morphology of the fibers with microscopic diameters turned out to be rather interesting (Fig. 6). In addition to the transversal nano-folds created by the transversal gradients of the speed of the solidification of the fibers the walls of the fibers demonstrated the presence of the nano-channels directed from the surface into the depth of the fiber. The diameters of the channels did not exceed 100 nm. The surface density of the channels was rather high – up to $10^9$ of the channels per square cm of the lateral surface of the fiber.

This new fact of creation of nano-channels in the composite fibers from polystyrene impregnated with particles of cesium iodide is interesting from at least two sides. The first one concerns the practical needs of effective utilization of radio-active cesium and iodine residual
Figure 6. The electron microscopy of the polystyrene fiber pulled out from the solution of polystyrene in benzene doped with nanoparticles of cesium iodide. The nano channels formed during the pulling out the fiber are seen clearly.

materials which are present usually in the cooling water of the nuclear plants. In the case of any accidents at these plants these radioactive remnants penetrate into the environment, so their utilization is sharply actual ecological problem [9–14]. Our polystyrene fibers impregnated with cesium iodide promise to be highly effective absorbers of radioactive cesium and iodine due to their active interactions with these materials and on the other hand due to high density of nano-channels providing big effective area of the active surface. It is worth to emphasize that this way of creation of nano-poured polymer materials is much more economic in comparison with well known method of preparation of nano-membranes by means of nuclear irradiation [19, 20].

On the other hand, understanding of the mechanism of this new phenomenon of auto-generation of the nano-channels in compositions organic-inorganic in addition to economic profits is capable for the generation of new knowledge about the interactions between these two kinds of materials. We assume that the main factor of this process is connected with the deformation activated creation of new kinds of interatomic bonds and corresponding atomic-molecular structures from cesium iodide and its constituents separately as well as of carbon and hydrogen. For example, deformation stimulated synthesis of hydrogen iodide can create nano-channels produced by the gaseous HJ exiting from the internal regions of the fibers. So two deformation activation factors can work in the case of the fibers being pulled out: the surface tension when the solution is transformed from the bulk state to the thin jet and the pressure from the bubbles of the gaseous hydrogen iodide. The joint action of these two factors is capable to induce the avalanche-like process of the deformation-chemical transformations.

Conclusions
A set of the experimental facts is presented justifying the version that the super-fast and super-deep introduction of foreign substances into crystals by the ball rolling proceeds by means of the sequences of openings and closings of the nano-cracks capturing the introducing substance at the stage of opening.

The formation of nanostructured channels in the fiber compositions from polystyrene and cesium iodide nanoparticles has been found during pulling out the fibers from solutions of polystyrene in organic solvents doped with nanoparticles.

The both of the processes described above are ascribed to the deformation activation of the intense chemical interactions between cesium iodide and the components of the organic
substances. The possibility of the preparation of new kinds of materials (inorganic crystals with containing dopants from organic molecules immersed into them) has been confirmed experimentally.

The new cheap technology has been demonstrated of the preparation of the nets of polymer fibers with high density of nanoscopic channels capable for effective adsorption of hazardous impurities (e.g. radio-active ions of cesium and iodine in wastes of nuclear fission).

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