Possibility of creating composite materials with self-diagnosis function based on the effect of mechanoluminescence

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Abstract. The increasing productivity of modern information processing systems opens up new possibilities for various technical devices. The ability to very quickly analyze a large amount of information allows you to constantly improve technical systems, including autonomous ones. Sensors or primary converters are used to obtain information about the surrounding world or external influences in technical systems. However, modern technologies make it possible to create materials with desired properties - composite materials. The programmable properties of materials can be strength, rigidity, resistance to mechanical, chemical and temperature influences, but it is especially worth noting the possibility of obtaining materials with specified informative properties. These materials include composites containing mechanoluminescent substances. Such materials can simultaneously be housings of any devices or enclosing structures, they can be parts of load-bearing structures of buildings and structures and at the same time play the role of shock and destruction sensors. Using such materials, you can create panels with a self-diagnostic function.

1. Introduction
Mechanoluminescence is the radiation of solids caused by mechanical action [1,2]. Based on this physical phenomenon, it is possible to design sensors for recording various external influences (impacts, slippage, deformation, cracking, destruction). Due to the optical nature of their functioning, mechanoluminescent sensors have certain advantages over other types of sensors. These advantages are: generator mode of operation; lack of sensitivity to electromagnetic interference; solidity; the ability to apply on surfaces of different shapes and areas; the possibility of embedding in a structure or embedding in a construction material. In some works [3-6], it is proposed to create mechanoluminescent (or triboluminescent) damage sensors. The range of applications for materials with mechanoluminescent properties is very wide. They can be used in construction to monitor the state of various supports or structures [7], to monitor the integrity of the hulls of mobile objects and robots [8] and to monitor the condition of the skin of aircraft [9].

2. The mechanism of luminescence
When luminescence is excited, an atom (molecule), absorbing energy, passes from the ground energy level 1 (figure. 1) to the excited level 3. As a rule, the emission level 2 lies below level 3, part of the energy is lost during excitation into heat, and the wavelength of the emitted more light than absorbed (Stokes luminescence). Processes are also possible when an emitting atom receives additional energy from other atoms; then the emitted quantum can have a shorter wavelength (anti-Stokes luminescence) [10, 11].
Figure 1. Scheme of quantum transitions in the elementary process of luminescence: 1-the main energy level; 2-the radiation level; 3 – the excitation level. The dotted line indicates the transition corresponding to resonant luminescence, and the wavy line indicates a non-radiative transition.

The emission level can belong to the same atom (molecule) that absorbed the excitation energy (such transitions are called intra-center), or to another particle. The transfer of energy to other atoms and molecules is carried out by electrons during electron-ion shocks, during ionization and recombination processes, by inductive resonance or exchange, when an excited atom directly collides with an unexcited one. Finally, energy transfer via conduction electrons, holes, and electron-hole pairs (excitons) becomes crucial in crystals. If the final act of energy transfer is recombination, then the luminescence accompanying this process is called recombination [10].

In the vast class of substances that have the ability to luminesce in general and to mechanoluminescence in particular, a special place is occupied by substances united under the general name “crystal phosphors” (CF). In CF, luminescence occurs due to the presence of a small amount of impurities of other substances called activators. Crystal phosphors are: sulfides (ZnS, CdS), selenides (ZnSe), silicates (Zn$_2$SiO$_4$), tungstates (CaWO$_4$), molybdates, and some other compounds [11]. Zinc sulfide CF have the highest luminosity [10] and make up more than 80 % of all industrial electroluminesphores [11]. It is for this reason that the vast majority of mechanoluminescence studies are conducted on ZnS phosphors.

3. Necessary conditions for mechanoluminescence

Explorations [12] showed that mechanoluminescence in A$_2$B$_6$ compounds is a consequence of the processes of motion and multiplication of dislocations accompanying plastic deformation of crystals. It was found experimentally that dislocations in A$_2$B$_6$ semiconductors, and in particular in ZnS, have a strong electric charge [8]. In the process of plastic deformation, the luminescence centers interact with the electric field of moving charged dislocations, which leads to the excitation (ionization) of luminescence centers with their subsequent radiative transitions.

To create a material with a self-diagnostic function based on the phenomenon of mechanoluminescence, it is necessary to ensure the hardness of the material. This condition is necessary for the energy of mechanical action to reach the crystals of the mechanoluminophor. As a result of this, plastic deformation of the crystals of the luminescent substance will occur, which will allow the luminescence mechanism to be triggered at the energy level.

Another important parameter of a material will be its optical properties. The optical parameters of a mechanoluminescent sensitive element, which determine the transfer of radiation in it, primarily depend on its structure. In the most common simplest case, the SE structure is a plane-parallel light-scattering layer of particles of a powdery luminescent material in a hardened transparent binder [8]. Such a layer is deposited on a substrate of a transparent material, which ensures, firstly, the creation of a stressed state of the particles during propagation of a pressure pulse (mechanical stress waves) through the layer, and secondly, the removal of radiation to the photodetector. Epoxy, melamine formaldehyde and other resins, varnishes, polystyrene and other transparent materials are used as a binder for powder phosphors [13]. Faceplates made of various glasses, optical ceramics, fiber-optic bundles and cables, tapers can be used as a substrate [8].

4. Methods for receiving composite materials with self-diagnostic function

As described above, in order to function, the mechanoluminescent sensor element embedded in the composite panel must be in a stressed state and it must be possible to output optical radiation from the sensor. A composite panel can be a rigid structure made up of several layers (figure. 2).
As a result of experiments [9] with panels of this configuration, the following frames of the glow of the phosphor were obtained (figure 3).

a) impact of a metal ball falling from a height of 0.5 m on a steel plate 1 mm thick;

b) the impact of a metal ball falling from a height of 1 m on a steel plate 1 mm thick;

c) the impact of a metal ball falling from a height of 0.5 m on a steel plate with a thickness of 2 mm;
d) the impact of a metal ball falling from a height of 1 m on a steel plate with a thickness of 2 mm;

e) the impact of a metal ball falling from a height of 1 m on a steel plate with a thickness of 6 mm;

**Figure 3.** Luminescence patterns of the distributed sensor at different impacts and shell thicknesses.

Another way to obtain a composite panel is to apply a mechanoluminophor to a transparent base in a vacuum [14]. This method consists in blend composed of bis (isopropylxanthogenate) ((2,2′-bipyridyl) zinc and bis (isopropylxanthogenate) ((2,2′-bipyridyl) manganese in 1000:(1-20) molar ratio is heated at evaporator temperature of 110-130 C, vapors are transferred and thermal decomposition is carried out in vacuum of $1 \times 10^{-5}$ to $1 \times 10^{-6}$ torr at substrate temperature of 150-300 C.

It is also possible to create composite materials with a self-diagnostic function based on the phenomenon of mechanoluminescence by introducing optical fibers with lateral light transmission and manganese-activated zinc sulfide grains into the material. The addition of mechanoluminescent materials to the epoxy compound and the creation of a structure that provides radiation transmission through optical fibers to the photodetector system allows solving the problem of monitoring and self-diagnostics of composite structures [13, 4]. An example of a composite material with built-in mechanoluminescent sensory areas and lateral light transmission optical fibers is shown in figure 4.

**Figure 4.** The implantation of a mechanoluminophor with an optical fiber with lateral radiation input into optical fibers in the composition of a composite material.
Distributed optical fiber systems and mechanoluminescent materials with different radiation spectra are used here for reliable recognition of a specific damage site [8].

5. Conclusions
A promising area of application of mechanoluminescent sensor elements is the development of composite materials and structures with the property of self-diagnostics [8,15]. On the whole, composites are materials consisting of carbon-graphite or quartz fibers embedded in epoxy compounds [12]. Such materials have high strength and stiffness with low weight and radio transparency. Currently, composites in the form of panels are widely used in mechanical engineering, aircraft and rocketry, in the construction of bridges, sports facilities, and others.

In addition to those given at the beginning of the article, as a positive property, it is worth noting the presence of a threshold nature of the dependence of the glow intensity on the applied mechanical effect. This ensures that the sensors are insensitive to minor loads and vibrations during operation. Integration of functions within a single structure allows the creation of built-in sensitive elements (sensors) that have the ability to selectively determine both the degree of damage to the composite panel and the specific location of the damage.

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