Cracking of composite scintillators after significant doses of irradiation

V.L.Cherginets[1], N.Z.Galunov[1,2], B.V.Grinyov[1], N.L.Karavaeva[1], A.V.Krech[1], L.G.Levchuk[3], V.F.Popov[3]

[1]Institute for Scintillation Materials, STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Nauky Ave., 61072 Kharkiv, Ukraine
[2]V.Karazin Kharkiv National University, 4 Svobody Sq., 61022 Kharkiv, Ukraine
[3]National Science Center "Kharkiv Institute of Physics and Technology", 1 Akademicheskaya Str., 61108 Kharkiv, Ukraine

The possible main causes of the cracking of composite scintillators during irradiation, i.e. the effect on the sample in the irradiation zone of temperature and the atmosphere (altered by radiochemical reactions) we identified and investigated. At a slow pace of irradiation (100–200 Mrad and 0.2 Mrad/h), exposure to aggressive components of the medium in the irradiation zone, namely, nitric acid and possible products of its radiolysis, becomes the main one. At a high irradiation rate (250–550 Mrad 1500 Mrad/h) a substantial heating of the sample occurs due to its absorption of a large amount of energy, which creates the main effect on the cracking of composite scintillators in this case.

Keywords: Composite scintillators, radiation-resistant, high energy, cracking, radiation chemistry.

Определены и исследованы возможные основные причины растрескивания композиционных сцинтилляторов при облучении, то есть воздействие на образец в зоне облучения температуры и, атмосферы (измененной благодаря радиохимическим реакциям). При медленном темпе облучения (100–200 Mrad и 0.2 Mrad/h) основным становится воздействие агрессивных компонент среды в зоне облучения, а именно, азотной кислоты и возможных продуктов ее радиолиза. При быстром темпе облучения (250–550 Mrad и 1500 Mrad/h) основное влияние на растрескивание композиционных сцинтилляторов оказывает воздействие на них высоких температур в результате поглощения композиционным сцинтиллятором большого количества энергии.

Розтріскування композиційних сцинтиляторів після значних доз опромінення. *В.Л.Чергінець, М.З.Галунов, Б.В.Гриньов, Н.Л.Караваєва, А.В.Креч, Л.Г.Левчук, В.П.Попов.*
Визначено і досліджені можливі основні причини розтріскування композиційних сцинтиляторів при опроміненні, тобто вплив на зразок у зоні опромінення температури і атмосфери (зміненої завдяки радіохімічним реакціям). При повільному темпі опромінення (100–200 Mrad і 0.2 Mrad/h) основним стає вплив агресивних компонент середовища у зоні опромінення, а саме, азотної кислоти і можливих продуктів її радіолізу. При швидкому темпі опромінення (250–550 Mrad і 1500 Mrad/h) основний вплив на розтріскування композиційних сцинтиляторів має дія на них високих температур у результаті поглинання композиційним сцинтилятором великої кількості енергії.

1. Introduction

We developed the technological approach to make the composite scintillators, which allows us to create effective detectors of various ionizing radiation [1–4]. Composite scintillators are single crystal scintillation grains inside a transparent base that is usually a gel composition. Composite scintillators have a number of advantages compared to classical scintillators: they have a lower cost compared to single-crystal scintillators, less fire hazard compared to liquid scintillators, etc.

The relevance of this work is due to its focus on the use of new features that provide developed technologies for the manufacture of radiation-resistant composite scintillators with theoretically unlimited dimensions and a complex shape of the input window. The practical result of such research is the development and improvement of the technological aspects of obtaining new scintillation materials with improved characteristics that satisfy the requirements of a wide range of modern problems of radiation materials science and instrument engineering. In particular, this is the production of radiation-resistant materials for detectors of super-large flows of ionizing radiation operating in the conditions of the latest experiments in high-energy physics.

Earlier, we fabricated and studied composite scintillators based on the Sylgard-184 transparent dielectric gel composition containing inorganic grains GSO: Ce, GPS: Ce, Al_2O_3: Ti, YSO: Ce, and YAG: Ce [1–4]. The obtained composite scintillators, in a number of cases, withstood the maximum dose of radiation up to 550 Mrad (in water equivalent). The values of the limiting doses in the works [1–4] are because, at high irradiation doses, despite the preservation of the operability of scintillation grains, the samples cracked.

This work is devoted to the study of the causes of cracking of composite scintillators after irradiation with significant doses of radiation on a linear electron accelerator LU-10 at the National Science Center "Kharkiv Institute of Physics and Technology", Kharkiv, Ukraine.

2. Experimental

Single-crystal grains of Al_2O_3 were introduced into the Sylgard-184 dielectric gel composition and kept until complete polymerization for 24 h at a temperature of $T = 50\pm5°C$. The size of the introduced granules ranged from 1.5 to 2.0 mm. Samples were made thin, i.e. crystalline grains were lo-
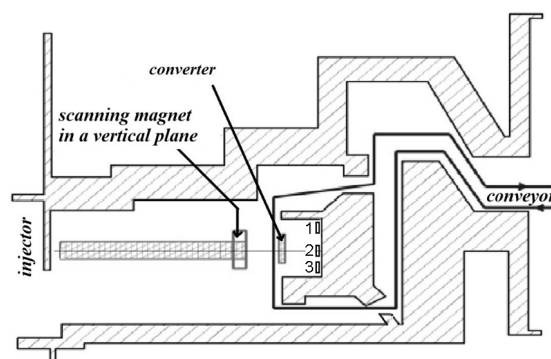

Fig. 1. Radiation map of dose loads in the experimental hall of the accelerator. For the positions of samples 1, 2, and 3, the dose rate is 0.12, 0.20, and 0.15 Mrad/h, respectively, and for the samples are directly on the conveyor in front of the injector, the dose rate equals 1500 Mrad/h.

cated in one layer on an area of 10×10 mm^2. In addition, for the studies, samples were prepared from the Sylgard-184 gel composition not containing scintillation grains with dimensions $20\times10\times4$ mm^3.

Irradiation we carried out for two different modes, namely, when the dose rate was 0.2 and 1500 Mrad/h. At a high irradiation rate, the samples were on the conveyor (Fig. 1), and as a result, the scintillators were within a short time in the area of the direct electron beam with an initial energy of about 10 MeV. During one pass in the front of the electron beam, which lasts 12 sec, the samples accumulate a dose of about 5 Mrad. After that, they moved with the conveyor outside the irradiation zone, being there for 40–50 min, until the next passage in front of the electron beam. At a low irradiation rate, the samples were placed in certain place in the experimental hall of the accelerator (see Fig. 1, position 2), where both electrons and bremsstrahlung were irradiating them. In this case, the scintillators were constantly in the irradiation zone until they had accumulated the required dose.

After irradiation, composite scintillators may crack due to the following main reasons [5]:

— the effect of temperature on the sample in the irradiation zone;

— the influence of aggressive atmospheric components (radiochemical processes).

The simultaneous action of these factors (synergistic effect) is also possible. Note that cracking of the samples appeared for a cumulative dose of 100 Mrad, when the ir-

radiation rate was 0.2 Mrad/h, and for a cumulative dose of 250 to 500 Mrad, when the irradiation rate was 1500 Mrad/h [1−4].

As noted above, the exposure time depends on the dose rate and determines the degree of influence of one factor or another on the process under consideration. Irradiation of composite scintillators for approximately 500 h, at the irradiation rate of 0.2 Mrad/h, will lead to the accumulation of a dose of 100 Mrad. At the irradiation rate of 1500 Mrad/h, the irradiation time to a dose of 500 Mrad is 20 min. Therefore, in order to accumulate a certain dose of D in the former case, it is necessary to irradiate the sample longer than in the latter. During irradiation, thermal expansion of composite scintillators can occur due to the absorption of a large amount of energy. The coefficients of thermal expansion of scintillation grains and gel compositions are different. As a result, the scintillator can crack along the defective regions formed during the polymerization of the base at the interface between the gel composition and grain [6].

During irradiation, thermal expansion of composite scintillators can occur due to the absorption of a large amount of energy. The coefficients of thermal expansion of scintillation grains and gel compositions are different. As a result, the scintillator can crack along the defective regions formed during the polymerization of the base at the interface between the gel composition and grain [6].

As applied to this work, the effect of temperature is much more likely for a high irradiation rate. At the beginning, the scintillator was sharply heated for 12 s under a direct electron beam, and then it gradually cooled down for 40−50 min. E.g., to set a dose of 250 Mrad, composite scintillators were running 50 cycles of such a sharp heating and gradual cooling. For a dose of 500 Mrad, 100 such cycles are necessary, which in turn can increase the likelihood of thermal expansion and, as a result, cracking of the sample.

With the low irradiation rate, the scintillators are practically at room temperature, i.e. the irradiation power does not sufficient to heat them up. Therefore, this effect is less likely than with the high irradiation rate.

The process of irradiation of composite scintillators takes place in the surrounding atmosphere, which initially contains 78 vol.% nitrogen, 21 vol.% oxygen and 1 vol.% of other gases (water vapor, CO_2, etc.). Therefore, ionizing radiation affects not only the composite scintillator, but also on compounds that are in the air. In other words, not only compounds in the source air, but also products of radiochemical reactions involving these substances can cause cracking of composite scintillators during irradiation. E.g., under the action of ionizing radiation on water vapor, its radiolysis leads to the appearance of the following main products:

$$H_2O \rightarrow \qquad (1)$$
$$\rightarrow H^0, H_2, O^0, O_2, O_3, OH^0, H_2O_2, HO_2^0, OH^-, H_3O^+.$$
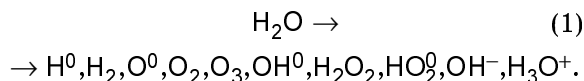
The most active of them are O_3, H_2O_2, HO_2, OH^- and H_3O^+ [5]. Under the action of radiation, ionization of substances occurs, and because of which radicals and ions absent before irradiation can form.

3. Results and discussion

After prolonged exposure at the low rate of irradiation, a certain liquid gradually forms on the surfaces and around the composite scintillators. The pH control using a universal indicator shows that this liquid has a pH about one, i.e. it is a strong acid solution. At the high rate of irradiation, no liquid appears around the samples. It is most likely due to both a weak manifestation of the effect itself and the high temperature of the scintillators during their passage through a beam of charged particles. The latter could well contribute to the evaporation of the resulting liquid.

To test the effect of acids on the cracking of samples of composite scintillators based on the Sylgard-184 gel composition, the following experiment we conducted. The following four acids we selected: H_2SO_4, HCl, H_3PO_4, and HNO_3. Samples of composite scintillators and gel compositions Sylgard-184 we placed in concentrated aqueous solutions of these acids.

Sulfuric acid dissolved the polymer base of composite scintillators without cracking. The first signs that acid dissolves the sample appeared after an hour. After 72 h, the degree of dissolution reached 90 %.

In solutions of HCl and H_3PO_4 acids, we did not observe any visible effects of acid action on the composite scintillator. The gel composition and composite scintillators remained elastic, even after a few months.

Composite scintillators cracked only when placed in nitric acid. Table shows the stages of this process.

Table presents the estimated values of the dose of D_{calc}, which the composite scintillator can receive at a low irradiation rate

for the time during which it was in acid. For comparison, Table also shows the values of the experimental dose of D_{exp} (irradiation at the same low radiation intensity) at which the concrete effect is manifesting. The nature of the destruction of samples in acid solutions indicates that during irradiation both nitric acid vapours and its radiolysis products affect scintillation samples. Note that $D_{calc} < D_{exp}$. This, as one would expect, indicates that the effect of the acid on the sample, when completely immersed in the acid, becomes stronger than when the sample is in acid fumes or its radiolysis products.

To exclude the presence of a solution of sulfuric acid after irradiation, we performed a qualitative analysis for the SO_4^- washout of this liquid using the following reaction.

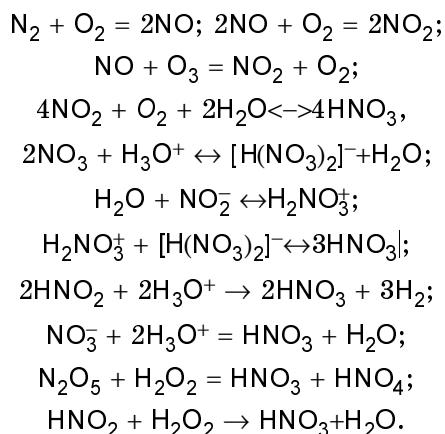$$BaCl_2 + H_2SO_4 \rightarrow 2HCl + BaSO_4\downarrow.$$
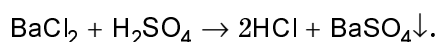
In our case, the formation of $BaSO_4$ precipitate did not occur, i.e. acid H_2SO_4 in the test solution is absent. To confirm the presence of nitric acid appeared in the solution after irradiation, we carried out a qualitative analysis for the NO_3^- ion.

$$2HNO_3 + H_2SO_4 + Cu \rightarrow$$
$$\rightarrow CuSO_4 + 2H_2O + 2NO_2\uparrow.$$
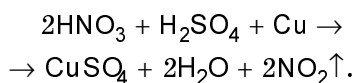
During this reaction, we observed the evolution of brown gas (NO_2). Thus, the presence of a solution of nitric acid, which appears during irradiation, can be considered proven.

As shown above, nitric acid forms during irradiation of composite scintillators. Due to the fact that the nitrogen content in the atmosphere is 78 vol.%, and oxygen — 21 vol.%, The following reactions are possible in the presence of water vapour:

$$N_2 + O_2 = 2NO; \ 2NO + O_2 = 2NO_2;$$
$$NO + O_3 = NO_2 + O_2;$$
$$4NO_2 + O_2 + 2H_2O <\!-\!> 4HNO_3,$$
$$2NO_3 + H_3O^+ \leftrightarrow [H(NO_3)_2]^- + H_2O;$$
$$H_2O + NO_2^- \leftrightarrow H_2NO_3^+;$$
$$H_2NO_3^+ + [H(NO_3)_2]^- \leftrightarrow 3HNO_3\downarrow;$$
$$2HNO_2 + 2H_3O^+ \rightarrow 2HNO_3 + 3H_2;$$
$$NO_3^- + 2H_3O^+ = HNO_3 + H_2O;$$
$$N_2O_5 + H_2O_2 = HNO_3 + HNO_4;$$
$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O.$$

These reactions are only an example of the possible pathways for the formation of nitric acid and intermediates. Under the influence of ionizing radiation, reactions can also occur, with the formation of other intermediate compounds. In this regard, it is important that the chemical activity of intermediate compounds, such as NO_2, N_2O_5, is quite high (see, e.g., [7]). From the experiment with acids (see above) it follows that it is the intermediate compounds and nitric acid vapours that interact with composite scintillators during irradiation.

According to [8], in a polymer base, chemical destruction can occur under the action of acids. Actively acting chemical agents are oxidizing acids (chromic, concentrated nitric and sulfuric acids), which cause the destruction of polymers (sometimes within a few minutes). E.g., under the action of concentrated nitric acid on polymers, oxidation (formation of carbonyl groups) and nitration (formation of nitro groups) occur simultaneously. Mineral acids (hydrofluoric, hydrochloric, dilute nitric and sulfuric, phosphoric, etc.) are less reactive with respect to polymers in comparison with oxidizing media. They practically do not affect polymers [8].

This confirms our experimental results, namely, hydrochloric and phosphoric acids did not react with the polymer base of the composite scintillator, sulfuric acid began to dissolve it within an hour, and treatment with nitric acid led to cracking.

At the same time, the results of the effect of nitric acid obtained without irradiation (under laboratory conditions) and upon irradiation (on a linear electron accelerator) are somewhat different (see Table). Most likely, this is due to several factors. Firstly, under radiation conditions, nitric acid, and its accompanying compounds, cannot affect the basis of the composite scintillator constantly, since ionizing radiation not only contributes to the creation of such compounds, but may also destroy them. Another factor relates to the effect of ionizing radiation itself on the polymer base [9]. In polymers under the influence of ionizing radiation, deep chemical changes occur. Such radiation can cause bond breaks in the polymer chain. However, this is not always due to redistribution and dispersal of energy. E.g., during the irradiation of polyethylene, only about 5 % of the absorbed energy causes chemical reactions, and 95 % turns into heat [9–11]. Under the action of high-energy radiation, not only destruction

Table. Comparison of the estimated values of the dose D_{calc}, which can lead to the observed effects, for composite scintillators immersed in nitric acid, with experimental values of D_{exp}

Stage	Effect description	Time in acid, h	D_{calc}, Mrad	D_{exp}, Mrad
1	Elasticity reduction	120	24	50
2	Cracks appear when bent, but a sample does not break	240	48	100
3	Manifestation of fragility (breaks under a small impact)	480	96	150
4	A sample become brittle (crumble when touched)	720	144	200−250

but also crosslinking of polymer chains occurs [9]. The crosslinking process of the polymer base can lead to the restoration of the integrity of the polymer chain and thereby increases the time before cracking.

4. Conclusions

Upon reaching the values of the limiting doses presented in [1−4], namely, 100−200 Mrad at the low dose rate and 250−550 Mrad at the high dose rate, cracking of composite scintillators occurs. However, the relative light output remains practically unchanged.

Possible main causes of cracking of composite scintillators because of irradiation in the atmosphere are (i) the effect of temperature on the sample in the irradiation zone and (ii) the effect of the atmosphere in the irradiation zone (radiochemical reactions). Both factors will depend on the time and the dose rate.

The cracking of the composite scintillator at a high irradiation rate is primarily due to the effect of high temperatures that occur when a large amount of energy is absorbed by the composite scintillator. In this case, the scintillator can crack along the defective regions formed during the polymerization of the base at the interface between the gel composition and grain.

At the low rate of irradiation, the surrounding atmosphere in the irradiation zone has a significant effect on the cracking of composite scintillators due to radiochemical reactions occurring in it. Shown, that the main aggressive components, the action of which leads to cracking of the composite scintillator, are nitric acid and possible products of its radiolysis.

The results obtained indicate that there is a possibility of increasing the radiation resistance of composite scintillators. For this, it is necessary to develop a technology for protecting the polymer base from the action of an external aggressive environment, e.g., by searching for protective coatings.

References

1. A.Yu.Boyarintsev, N.Z.Galunov, Ia.V.Gerasymov et al., *Nucl. Inst. Meth. Phys. Res., A*, **841**, 124 (2017).
2. N.Z.Galunov, T.E.Gorbacheva, B.V.Grinyov et al., *Nucl. Inst. Meth. Phys. Res., A*, **866**, 104 (2017).
3. N.Z.Galunov, Ia.V.Gerasymov, T.E.Gorbacheva et al., *Probl. Atom. Sci. Techn., Ser.:Nucl. Phys. Invest.*, No.3, 35 (2017).
4. A.V.Krech, N.Z.Galunov, *Ukr. J. Phys..*, **62**, 569 (2017).
5. A A.Mazunder, Fundamentals of Radiation Chemistry, Academic Press, San Diego, London, Boston, Ney York, Sydney, Tokyo, Toronto (1999).
6. T.E.Gorbacheva, *Functional Materials*, **21**, 290 (2014).
7. E.Davydov, I.Gaponova, G.Pariiskii et al., *Chem. Chem. Technology*, **4**, 281 (2010).
8. E.N.Cherezova, N.A.Mukmeneva, V.P.Arkhireyev, Aging and Stabilization of Polymers. Part 1: Study Guide, Kazan: Kazan Publishing House, National Research Technological University (2012) [in Russian].
9. V.P.Arkhireyev, Aging and Stabilization of Polymers, Kazan. Gos. Tehnol. U-nt, Kazan (2002) [in Russian].
10. Radiation Chemistry of Macromolecules, Atomizdat, Moscow (1978) [in Russian].
11. F.A.Mahlis, Radiation Physics and Polymer Chemistry, Atomizdat, Moscow (1972) [in Russian].