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Development of material and method for 3D printing an absorber for a sampling detector

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A new method for creating an absorber for a sampling detector using 3D printing technology on an FDM printer is proposed. A prototype of the absorber was manufactured using the proposed method. Alloys of bismuth, lead, tin and cadmium are proposed as absorber materials. The alloys studied are close to lead in their absorption properties; at the same time, they have a melting point that allows their use in 3D printing together with polymeric materials, avoiding high temperatures. It is experimentally shown that the selected material and method can potentially be used to form an alternating scintillator-reflector-absorber structure in a single technological cycle. The proposed method can be useful in the development of sampling detectors with improved energy resolution.

Keywords: absorber, sampling detector, alloy, scintillation element, 3D printing, composite material.

Розробка матеріалу та методу 3D друку абсорберу для гетерогенного детектора. *М. Сибілєв, С. Барсук, А. Бояринцев, А. Карбон, О. Колесніков, Т. Сібілєва*

Запропоновано новий спосіб створення абсорбера для гетерогенного детектора з використанням технології 3D друку на FDM принтері. За запропонованим способом виготовлено дослідний зразок абсорбера. Як поглинаючі матеріали пропонуються сплави вісмуту, свинцю, олова і кадмію. Досліджені сплави близькі до свинцю за своїми абсорбційними властивостями, і в той же час мають температуру плавлення, що дозволяє використовувати його в 3D-друці разом з полімерними матеріалами, уникаючи надмірних температур. Експериментально показано, що вибраний матеріал і спосіб потенційно можуть бути використані для формування в єдиному технологічному циклі змінну структуру сцинтилятор-рефлектор-поглинач. Запропонований метод може бути корисним при розробці гетерогенних детекторів з покращеною енергетичною роздільною здатністю.

1. Introduction

Calorimeters are widely used in high energy physics to measure the energy and position of particles, and to identify particles. They are designed to completely absorb the particle energy in the detector volume and produce a signal proportional to the initial energy of the particle. Homogeneous calorimeters represent a monolithic mass of scintillation material, which serves simultaneously to develop a shower and to detect a signal. In sampling calorimeters, these two functions are performed by different materials. Several sampling (heterogeneous) technologies employ alternating plates of scintillation tiles (detecting layer) and absorbing layer. A reflecting layer between the scintillator and absorber plates improves the signal yield by effectively retaining the light in the scintillator until it is transported to the photon detector typically via wavelength shifting (WLS) fibers that run throughout the calorimeter. Traditionally, heavy absorbing materials are used: lead [1] iron [2], copper [3, 4], steel [5], tungsten [1], uranium [6]. There are well-known examples of such typical sampling detectors: Shashlyk [2, 7], SpaCal [8], and TileCal [9], at the LHC calorimeters at CERN.

Sampling calorimeters can be adapted to specific requirements through the choice of detecting and absorbing layers, both material and geometrical design; they can be compact by choosing high-density absorber materials; both lateral and longitudinal granularity can be achieved. In addition, sampling calorimeters are more cost-effective compared to the homogeneous ones.

Although sampling calorimeters have been in use for several decades, they continue to evolve. In particular, their energy resolution can be improved by reducing the sampling via the use of thinner absorber layers with a corresponding increase in the number of detecting scintillation layers [10, 11].

Sampling calorimeter production is so far performed via manufacturing of individual components: scintillation tiles, absorber plates, sheets of reflecting material, and hand-assembling them into multilayer modules. However, as the thickness of the layers decreases, the effect of thickness or density variations creates a visible impact on energy or spatial resolution. In addition, the labor load of detector fabrication also increases. Therefore, 3D printing as an alternative method of detector manufacturing promises to eliminate the complexities of multistage production and develop technology for the efficient production of prototypes with various geometries. Our previous investigations [12, 13] have shown that plastic scintillation detectors with a reflective layer manufactured by 3D printing in a single technological cycle is competitive to detectors produced by conventional technologies of mass polymerization, injection molding or extrusion.

This work proposes to develop a prototype absorber suitable for a sampling detector, completely manufactured by a 3D printing.

2. Experimental

2.1. Absorber requirements

The choice of the material is motivated by the requirement of an efficient absorption. The absorption qualities are determined by the following parameters:

1) density;

2) small radiation length (X_0) that depends on the large value of atomic number Z or Z_{eff} for compounds and mixtures.

Other important requirements to the absorber material is its resistance to the effects of ionizing radiation, which ensures the mechanical stability of the absorber, and a tolerable level of radiation induced in a material in order to maintain the corresponding background counting well below the physics counting rate.

Radiation length (X_0) characterizes the energy loss in the absorber (the distance at which the energy of an electron decreases by a factor of '*e*'). According to [6], the radiation length:

$$X_0 \approx \frac{716.4 gcm^{-2} A}{Z(Z+1) Ln(287/\sqrt{Z})} \quad (1)$$

where A is the mass number, Z_{eff} is the effective atomic number.

In turn, Z_{eff} is related to the interaction of radiations inside this environment. According to [14], Z_{eff} for mixtures and compounds is determined by the formula:

$$Z_{eff} = \sqrt[2.94]{f_1 \times (Z_1)^{2.94} + f_2 \times (Z_2)^{2.94} + f_3 \times (Z_3)^{2.94} + \cdots} \quad (2)$$

where f_n is the fraction of the total number of electrons associated with each element, and Z_n is the atomic number of each element.

So, the main requirement for the absorber material is a short radiation length. For this purpose, it must have a large Z_{eff}/A ratio and high density.

2.1. Materials and methods

The method used for additive manufacturing of parts is FDM (Fused Deposition Modelling) 3D printing technology, which is based on layer-by-layer deposition of molten material on the work platform. A thread of fusible material (filament) is fed into a heated extruder, melted and squeezed onto the platform. The extruder moves along a predetermined trajectory, creating a part of a given shape.

Printing a prototype of a sampling detector element involves the alternate creation of a structure consisting of three layers: scintillator, reflector and absorber. The printing format is the shaping of layers in a single technological process with three different materials.

The scintillation layer was printed with a standard diameter filament of 1.75 ±0.05 mm, produced by a previously reported method [12, 13] from polystyrene-based material with addition of 2% (by weight) of paraterphenyl (pTP), 0.05% (by weight) of 2,2-p-phenilene-bis(5-pheniloxazole)) (POPOP) and 5% (by weight) of biphenyl.

The reflective layer was printed with a standard diameter filament of 1.75 ±0.05 mm [12] from polystyrene-based material with addition of 20% (by weight) of finely dispersed filler TiO_2 and 1.5% (by weight) of dioctyl phthalate.

This work investigates a material for an absorbing layer that would provide absorption properties (radiation length and Z_{eff}) and a method for 3D printing with this material. Two alternative methods were considered to test the absorber production:

1) printing with a filament made of a composite material based on a plastic binder with a metal powder filler;

2) direct molten metal printing.

The criteria are the effective density and the uniformity of its distribution, the surface quality, and technological considerations.

Printing of the absorber with a composite material was realized using a commercially available *Rapid 3DShield Tungsten Filament* [15]. Also, for comparison, we manufactured our own filament using a previously developed method [16], based on a plastic binder thermoplastic polyurethane (TPU) filled with tungsten metal powder (W) 93.5% by weight (48% by volume) with the addition of 1.5% - 3.5% plasticizer (dioctyl phthalate).

The printing of the absorber directly by the metal melt was performed with a specially designed metal filament. For this purpose, an alloy composition (Bi, Pb, St, Cd) was selected, corresponding to the set of absorption parameters and physical properties. Weighted quantity of the starting metals was alloyed and homogenized in a ceramic crucible. The production of the alloy filament with a diameter of 1.8 ±0.05 mm for printing at an FDM printer was carried out by melt injection under pressure into a tubular mold (PTFE tube). The temperature of the mold was maintained above the melting point of the alloy.

The Noztek Pro HT extruder [17] was used for the production of scintillation and retroreflective filaments and a composite filament for absorber printing. The CREATBOT F430 3D printer [18] was used for printing samples.

2.2. Mechanical properties

The physical and mechanical requirements for the absorber printing material depend on the specific type of the alternative printing method discussed in this article:

- For a filament made of a composite material based on a plastic binder with a metal powder filler, it is important to maintain sufficient elasticity and fluidity in the molten state to be used for printing by an FDM printer extruder.

- For a metal alloy filament, the melting temperature is important. This is due to the fact that layer-by-layer creation of the part involves printing with metal melt on top of already formed layers of the plastic scintillator and reflector. To avoid damaging them, the temperature of the metal melt should not be too high. This imposes a limit on the upper value of the alloy melting temperature. It has been experimentally established that at the printing temperature close to the glass transition temperature of polystyrene (105÷109)°C [19, 20] there is no deformation of previously printed layers. When the printing temperature increases above (160÷180)°C, warping of polystyrene and the appearance of gas-filled bubbles under the printed absorber layer are observed. According to [21] the viscosity of polystyrene at such temperatures decreases to (10^3 ÷10^2) Poise. Apparently, such a value of viscosity is critical.

The lower limit of the melting temperature of the alloy is determined by the conditions of storage, transportation and operation of the equipment. We adopted it at the level of 70°C.

Another important property of a product created using the 3D printing method is the uniformity of its structure.

3. Results and discussion

3.1. Printing of absorber with composite material

To meet the requirements for the absorber, the task of developing a composite material filament was reduced to a combination of the following conditions:

1) Maximum filling of the plastic binder with high-Z and high-density metal powder;

2) Preservation of sufficient elasticity and fluidity of the resulting composite material in the molten form.

3) Resistance to ionizing radiation, to ensure mechanical stability of the absorber.

Tungsten (W) was chosen as the metal filler since this metal has suitable parameters

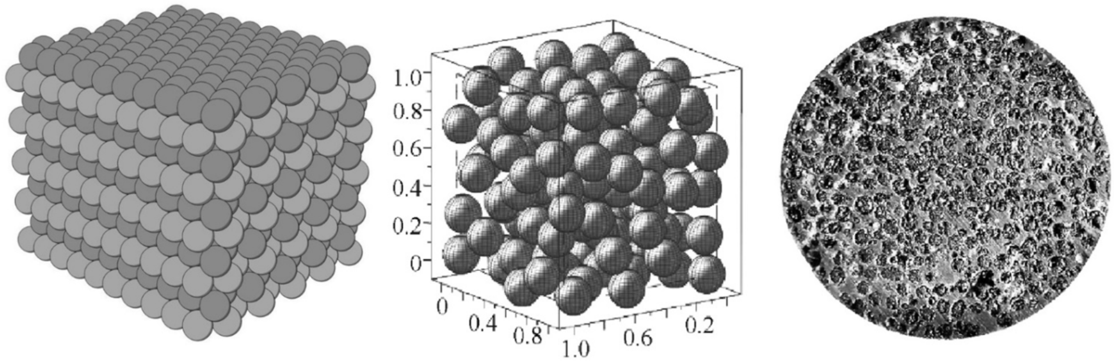

Fig. 1. (a) the principle of perfect densest packing of particles in space (figure “a” is taken from [23]), b) random close-packed system of monodisperse particles and c) example of particle distribution in composite material (figures “b” and “c” are taken from [24]).

Fig. 2. a) manufactured filament of composite material based on plastic binder PS filled with tungsten metal powder (W) and b) samples printed with it.

that affect absorption properties: density of 19.25 g/cm^3, atomic number Z =74 and radiation length of 6.76 g/cm^2.

Based on the principles of close-packing (Figure 1,a), if we accept the condition of spherical geometry of equal-sized particles, then the maximum possible coefficient of filling space with particles will reach a value of 74.05% [22]. At the same time, the calculated density of the composite with such filling could be up to 14.5 g/cm^3.

In practice, the space filling coefficient of spherical metal powders of the same size will reach a value of approximately 60% by volume [25]. This is the upper limit for the entry of equal-sized metal particles into the volume of composite material based on a polymer binder. Attempts to fill the polymer with a larger number of equal-sized solid particles lead to the lack of coherence of the material and its destruction. It is expected that at random distribution of particles (Figure 1 b, c), the coefficient of filling of filament and printed parts will be even lower.

Thus, the commercially available composite filament *Rapid 3DShield Tungsten Filament* [15] based on polylactide (PLA) with tungsten content up to 91-93% by weight (40-45% by volume) has a density up to 7.8 g/cm^3. The calculated Z value of the *Rapid 3DShield Tungsten Filament* is 35.4. Experimental data provided by the manufacturer shows that parts printed with this filament have a density of up to 6.8 g/cm^3.

A number of experiments were carried out to create our own filament from a composite material with a high content of tungsten powder. The filament was made on the basis of a plastic binder (TPU - thermoplastic polyurethane) with a filler of tungsten metal powder (W), with the addition of (1.5-3.5)% plasticizer (dioctyl phthalate) in a manner similar to that presented in our work [16]. It was possible to incorporate up to 93.5% by weight (48% by volume) of tungsten powder into the composite. The calculated density of this material was 9.8 g/cm^3. The actual density of the printed parts was up to 8.0 g/cm^3. This indicates that air enters the melt of the binder on the surface

Table 1. Compositions and parameters of the investigated alloys

#	% (mass)				Density, g/cm^3	Z_{eff}/A	Radiation length, g/cm^2	Radiation length, cm	T_m,°C
	Sn	Pb	Bi	Cd					
1	0.121	0.252	0.504	0.131	9.73	0.441	6.012	0.618	73
2	0.187	0.250	0.500	0.063	9.64	0.439	6.038	0,626	84
3	0.250	0.250	0.500	0.000	9.56	0.436	6.061	0.634	95
4	0.160	0.320	0.520	0.000	9.69	0.424	6.093	0.629	98
5	0.173	0.482	0.346	0.000	10.1	0.425	6.106	0.605	110
6	0.116	0.531	0.313	0.041	10.28	0.424	6.102	0.594	110
7	0	0.455	0.545	0	11.23	0.397	6.263	0.558	124
8	0.175	0.475	0.350	0.000	10.09	0.426	6.104	0.605	140
9	0	100	0	0	11.34	0.396	6.310	0.556	327
10	W 100 %				19.2	0.403	6.764	0.351	3422
11	Cu 100 %				8.96	0.457	13.15	1.468	1084

of tungsten particles and the uneven filling of the volume with the melt. Our printing experiments show that up to (10–12)% of the space in a composite part is not filled with material. The approximate Z_{eff} value for this material is about 38.9. However, the final density and uniformity of filling the volume of the part with material strongly depend on the printing conditions and printer settings.

The parameters of the filament we developed are slightly superior to the commercially available analogue: the practical density of the product material is 8.0 g/cm^3 compared to 6.8 g/cm^3 of the commercial sample, and the calculated Z_{eff} is 38.9 versus 35.4; however, the composite we obtained still cannot be an alternative to metals currently used as absorbers for sampling detectors. At the same time, our filament (Fig. 2, a) turned out to be more porous than the commercial analogue and had greater fragility and less homogeneous structure, which is predictably explained by a larger filling of the composite with solid particles and, accordingly, a decrease in the plastic binder. These properties do not allow it to be used as a starting material for the production of the detector absorber.

Test samples were printed as square plates with a side of 20 mm and a thickness of 1 mm (Fig. 2, b). The quality of the printed samples did not provide sufficiently smooth surface and geometric tolerances of the part. Also, the homogeneity of filling the part volume with metal particles when using this technology is not guaranteed.

One should not forget about the known degradation of polymer binders [26] used in composite materials. This may adversely affect the service life of the detector and the quality of registration of the detected parameters.

In the course of our work, we came to the conclusion that the capabilities of FDM filament printing of a composite material based on a plastic binder with a metal powder filler are insufficient for use as an alternative to the materials currently used in the production of absorbers for sampling detectors.

3.2. Selection of metal alloy for printing

After obtaining the results of 3D printing of an absorber with a composite filament, an alternative method of additively forming an absorber layer has been further developed. This is printing with a pure metal alloy. In fact, injection technology was used, implemented on the basis of an FDM printer extruder.

According to previously established criteria, the material for printing the absorber with a metal alloy must meet the following requirements:

1) high density;
2) small radiation length (X_0) that depends on the large value of Z_{eff};
3) melting temperature in the range of 70-110 °C.

To create the absorber material, alloys containing bismuth (Bi), lead (Pb), tin (St) and cadmium (Cd) were investigated.

The development of metallic materials for melt 3D printing was discussed in [27]. Similar compositions of metal alloys are also used as low-temperature solders, for example, the Lichtenberg alloy [28]. However, the eutectic alloys used have melting temperatures higher than required for the purposes of this work; the pa-

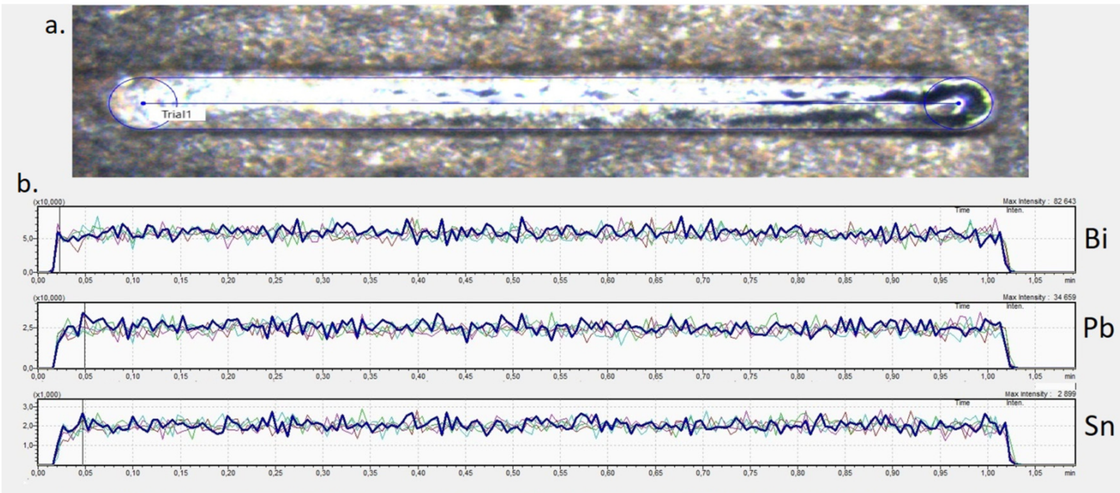

Fig. 3. a) sampling of materials by mass spectrometry with laser ablation; b) Results of measuring the uniformity of the distribution of elements within the alloy.

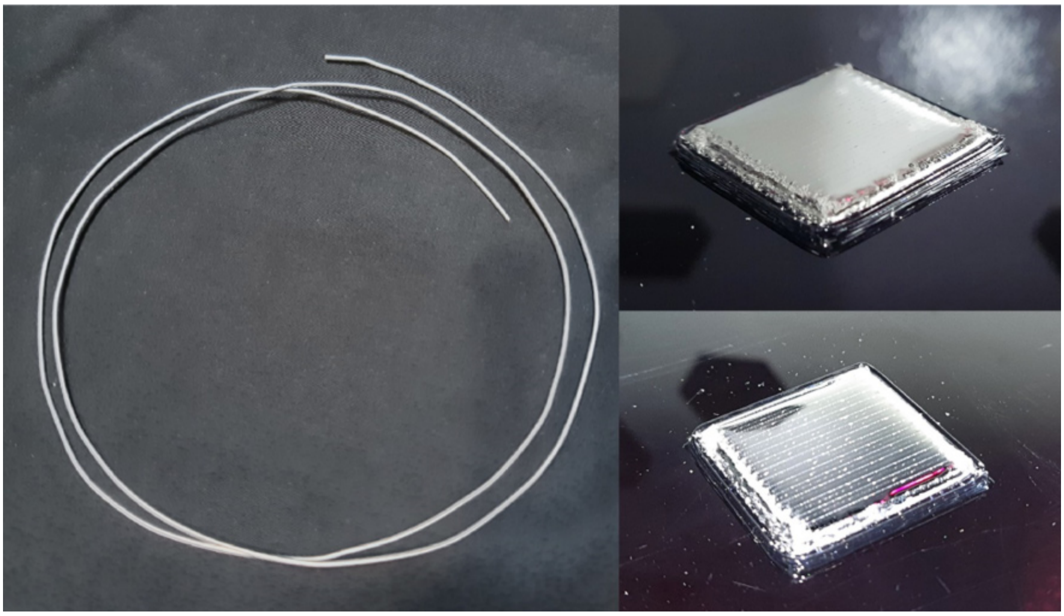

Fig. 4. (a) metal filament with a diameter of 1.8 ± 0.05 mm for printing on FDM printer and (b) printed samples of the three-layer structure scintillator, reflector, metal absorber.

rameters that ensure the absorption properties of the material (density, Z_{eff}, radiation length) were also not analyzed.

We investigated a number of alloys, the composition and parameters of which are given in Table 1. For comparison, the parameters of traditional materials used for manufacture of absorbers − lead, tungsten and copper − are given. It is seen that the density of the investigated alloys is 9÷15 % lower than that of lead. At the same time, the difference in radiation length is not so significant and for sample No. 5 in Table 1 is only 6 %. But, the proposed alloys are considerably inferior to tungsten both in density and radiation length. However, they turn out to be significantly better than copper by the same parameters.

The phase diagrams of the alloys under study were not constructed. However, we note that the difference between the temperatures of complete melting of solid phases (liquidus, T_L) and final crystallization of the alloy (solidus, T_S) for these alloys is up to 20°C. If the printing temperature is above the liquidus temperature, the metal remains liquid during the printing process. Under these conditions, a smooth surface can be achieved. However, this printing mode does not allow the production of complex shaped parts. In printing modes where the extruder temperature is between TL and TS, the

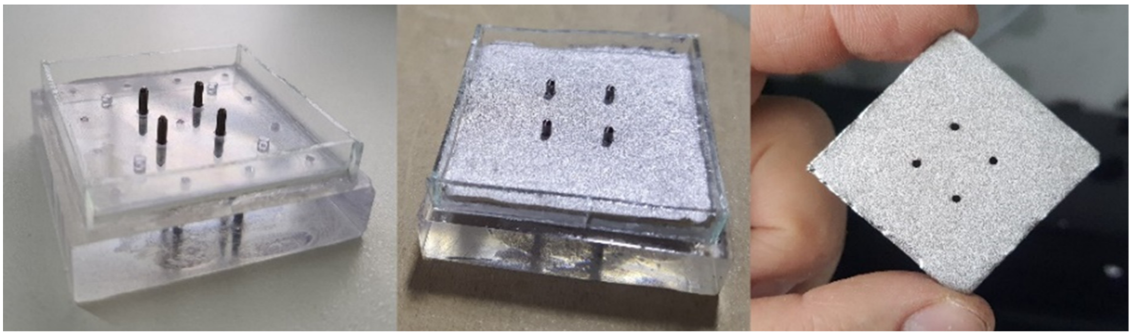

Fig. 5. Samples of metal absorber on polystyrene with the formation of holes for WLS fiber.

material exiting the nozzle is a viscous mixture of solid and liquid phases. Increasing viscosity allows you to obtain a product of a more complex shape, but its surface is less smooth.

In this work, the mechanical properties of melts of various compositions and their behavior during FDM printing were investigated.

3.1. Discussion

The sample of alloy No. 4 (Table 1) was chosen for printing prototypes because it has a relatively low melting point and does not contain cadmium. The presence of cadmium in the alloy is undesirable, since this metal has an exceptionally high ability to capture thermal (slow) neutrons, which can affect the detection properties of the sampling detector. The composition of 52% bismuth, 32% lead and 16% tin is a eutectic alloy of these three metals [29]. The eutectic point ensures rapid crystallization of the melt and, as a consequence, a more uniform distribution of solid solution elements. This ensures homogeneity of absorption properties.

The uniformity of distribution of elements in the absorber layer was measured using an ICPMS-2030 LF mass spectrometer with an ESL NWR213 laser ablation system. For this purpose, the separation of the alloy substance by a laser pulse was carried out along lines 600 µm long (Figure 3, a). The laser spot size was 50 µm and the scanning speed was 10 µm/s. The laser energy was set at 5%. The measurement results (Figure 3, b) showed that the distribution of elements inside the eutectic alloy is uniform.

Using the method described above in this article, a filament with a total length of up to 2 m was produced, satisfying the mechanical and geometric requirements of printing (Figure 4,a).

Printing of the samples shown in Figure 4, b was carried out in the following order. The first layer was printed with scintillation polystyrene (1.5 mm). Then the reflector layer (0.5 mm) was made. To prevent the molten metal from leaking outside the printing area, an additional 0.5 mm high border was printed around the perimeter using plastic filament. An absorber layer was printed as the third layer. The metal was distributed in a manner similar to conventional FDM printing. In this case, the entire metal layer was in a molten state during the printing process. This allows the absorber material to be evenly distributed over the entire surface of the part. At the same time, the metal layer is firmly connected to the plastic layer. No air gaps were observed between the layers.

The problem of forming holes for WLS fiber remains open, since the entire volume of the metal layer is in a molten state during printing. When printing at temperatures between liquidus (T_L) and solidus (T_S), the viscous mixture of solid and liquid phases in the melt allowed for the production of more complex shaped parts. However, the quality of holes with a diameter of about 1 mm was still unsatisfactory. The smoothness of the surface was also insufficient.

To solve this problem, the possibility of manufacturing a part with holes for light guide WLS fiber at the stage of additive forming was tested (Fig. 5). For this purpose, the method of pouring the part on top of scintillation polystyrene tile was used. The holes were formed by using shapers – rods with a diameter of 1.3 mm, made of nickel with a fluoroplastic coating (Ni-PTFE). After the melt solidified, the metal layer was easily separated from the rods. At the same time, as in the previous case, a strong bond was maintained between the metal layer and the plastic layer. Thus, this method showed the possibility of using rods coated with fluoroplastic-containing materials to create holes for light conducting fibers of satisfactory geometry.

4. Conclusions

The fundamental possibility to create prototypes of sampling detector absorber using 3D printing on FDM printer is demonstrated.

A comparison of absorber materials based on tungsten composite material in a polymer matrix and metal alloys with a low melting point was carried out. Alloys for absorber material based on bismuth, lead and tin are proposed. It is shown that the radiation length of the studied alloys is (0.596 - 0.64) cm. The best values approach the radiation length of widely used lead (0.56 cm). The proposed method can be useful in creating of sampling detectors with improved energy resolution. The fundamental possibility of creating all functional layers of a sampling detector in a single technological cycle of joint printing is demonstrated: a scintillator, a reflector and an absorber.

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