Chemical method of creation of effective Ni63 radiation source for betavoltaic converters

A T Lelekov¹,², N P Evsevskaya³, I V Kovalev²,⁴,⁵, P V Zelenkov⁶ and V V Brezitskaya²

¹ Federal Research Center "Krasnoyarsk Science Center of the Siberian Branch of the Russian Academy of Sciences", 50 Akademgorodok, Krasnoyarsk, Russia
² Reshetnev University, 31 Krasnoyarsky Rabochy Av., Krasnoyarsk, Russia
³ Institute of Chemistry and Chemical Technology, Federal Research Center "Krasnoyarsk Science Center of the Siberian Branch of the Russian Academy of Sciences", 50/24 Akademgorodok, Krasnoyarsk, Russia
⁴ Siberian Federal University, 79 Svobodny Pr., Krasnoyarsk, Russia
⁵ Krasnoyarsk State Agrarian University, 90 Mira Av., Krasnoyarsk, Russia
⁶ LLC KotHelper, 63-B Krasnoyarsky Rabochy Av., Krasnoyarsk, Russia

E-mail: a.t.lelekov@yandex.ru

Abstract. The article highlights the results of studying the parameters of nickel film chemical deposition on base aluminium foil, the purpose of which is to create an effective source of beta radiation Ni63 source for a betavoltaic converter. To increase the specific area of the source, it is proposed to micro-corrugate the base by rolling and laser fusion. Recommendations on the practical implementation of the source manufacturing are given.

1. Introduction

Recently, the development of technology for the creation of betavoltaic power sources has become very important. According to various forecasts, their possible application is quite large, such as medicine and healthcare (pacemakers, neurostimulators, bionic prostheses), industrial production and infrastructure (systems for monitoring the integrity of structures and pipelines, valve state monitoring systems, gas analyzers, identification marks), armaments and ammunition (security sensors, access control sensors, monitoring the status of a serviceman, listening devices), telecommunication equipment (systems portable devices, computer integrated systems), spacecraft and systems [1].

The use of Ni-63 isotope as a source with a half-life of 100 years makes the battery durable. In this case, the isotope radiation is very soft and low-energy. It is safe for human health, while providing protection against ingress of an isotope into the body.

In the most proposed constructions [2-11] the Ni63 isotope is either deposited directly on the betavoltaic converter or on a mechanical support and then applied to the converter.

In the second case, it would be logical to use aluminum foil as a base, since it is an easy to process and very affordable material, and also because of its chemical "compatibility" with nickel - if inadequate quality samples are obtained, the expensive nickel isotope can be returned by dissolving base in alkali.
The experiment used food-grade aluminum foil with a thickness of 9 μm (commercially available foils up to a thickness of 2 μm). Three variants of a base foil were studied, which differ in the microcorrugation method:

- without processing, the original flat foil was taken;
- microcorrugation by rolling the initial foil on uneven jewelry rolls;
- microcorrugation with laser, which make melt dots on foil surface;

Reagents containing stable (non-radioactive) isotopes of nickel are used in this research, since radioactive and non-radioactive isotopes have identical chemical properties due to the same structure of the electron shells of the atom.

2. Aluminum foil masking
The foil-based radiation source can be made one-sided. In order for nickel deposition to occur only on one side of the foil, a polymer mask for printed circuit boards was applied to the reverse side. Using this mask, you can create on the working side of the source a window of the desired shape.

The standard technology for applying a mask to a printed circuit board consists of washing the workpiece, applying a certain amount of mask material to PCB surface, rolling the mask with a soft roller through an intermediate polymer sheet. Then the mask is exposed, unnecessary areas are washed off in the solvent.

When applying the mask, the foil was applied to a solid base (2 mm textolite) and held by tape. The size of the base was about 200x300 mm. Then a mask was applied with a roller. After hardening of the mask, the surface of the foil remained flat. Modification of the technology and all masking experiments were carried out at SKTB "Nauka" of the Institute of Computational Modeling of SB RAS (Krasnoyarsk, Russia), by specialists from the PCB department.

The foil was cut into 30x10 mm pieces (corresponding to the size of a BNi3.S3.4R radiation source, manufactured by Ritverc, St. Petersburg, Russia) was performed on a MiniMarker2 laser engraving machine (20% power mode, cutting speed 100 mm/s).

3. Microcorrugation of the aluminum foil by rolling
When using jewelry rolling rollers, micro-corrugated aluminum foil can be obtained in several ways. The simplest of them is to apply a microrelief on the surface of the rollers, which will be printed on the foil during rolling. For this, various demands of changing the surface roughness are suitable, both complex (for example, electroerosive or electrochemical processing) and the simplest ones (sandling with sandpaper and grinding pastes). But in our case, we could not change the surface of the rollers.

Microcorrugated foil can be obtained by rolling it simultaneously with a softer and more heterogeneous material. For this we used thin paper, which is very heterogeneous on a microscale. Passing through the rollers, the paper fibers were crushed unevenly, creating a random relief on the foil (figure 1). By adjusting the pressure force of the rollers, laying paper of various thicknesses and structures, the surface relief of the foil can be varied. With too much force, the foil can tear.
4. Microcorrugation with laser
The microcorrugated surface on the foil can be created directly, for example by heating or even melting it pointwise. The same laser machine was used to cut the foil. At high radiation power, the laser burns the foil, creating a round hole with a diameter of about 100 microns (figure 2).

By reducing the laser power and changing the speed of the beam, it is possible to obtain fused points, the surface of which has a complex shape. The diameter of the dots decreases to 30-50 microns, compared with fully melted. Figures 3 and 4 show the surface of the foil with different dot densities. Obviously, the denser the points are located, the more developed the surface can be obtained.
5. Chemical deposition of nickel on aluminum foil

Chemical nickel plating was carried out according to the following procedure. The foil samples, the dimensions of which were 30x10 mm, were immersed in an electrolyte (the electrolyte composition is given in the table 1) and the process was conducted on an electric stove for a predetermined time at a temperature of 98°C. A 100 ml heat-resistant glass with a lid was used as a nickel-plating vessel. Before nickel plating, the samples were treated with ethanol.

Table 1. Electrolyte composition.

| Components       | Concentration |
|------------------|---------------|
| nickel sulphate  | 25 g/l        |
| sodium hypophosphite | 25 g/l       |
| thiourea         | 5 mg/l        |
| sodium acetate   | 10 g/l        |
| acetic acid      | 6.2 ml/l      |

The choice of electrolyte is due to the fact that a radioactive isotope suitable for nickel plating is easier to obtain in sulfate or chloride form, but the chloride electrolyte does not provide the desired coating. The process of spontaneous reduction of nickel in the solution volume is likely, which leads to decomposition of the electrolyte. To increase the stability of the electrolyte, thiourea was introduced into the composition. One of the main factors determining the speed of the process is the temperature of the solution. It is established that the process practically does not proceed at low temperature, optimal temperature is 96-98°C. A significant effect on the rate of chemical nickel plating process and the quality of coatings is exerted by the acidity of the solution, the best results are obtained at pH = 4.5-5.5.

All samples were processed in a sulfate electrolyte at 98°C, pH = 4.5. Processing time was 20-40 minutes (see table 2). Detachment of the polymer mask on all masked samples did not occur. In all experiments, nickel coating was released only on the surface of aluminum; no nickel coating was formed on a polymer mask and in the volume of the electrolyte or on the vessel.

Table 2. Investigated samples.

| No.   | Sample description                        | Processing time |
|-------|-------------------------------------------|-----------------|
| 5000  | Aluminium foil                            | 20 min          |
| 5001  | Aluminium foil                            | 40 min          |
| 5009  | Aluminium foil with a green polymer       | 20 min          |
| 5010  | mask on the back                          | 40 min          |
| 5030  | Aluminium perforated foil with mask       | 20 min          |
| 5031  | on the back                               | 40 min          |

Aluminum foil has a different structure on both sides, it is noticeable to the naked eye, one side is matte and the other is shiny. Microscopic examination revealed that this is due only to the microstructure of the foil. Commercially available foil does not have additional coatings (for example, a silicone layer), which means that no additional processing is required to clean the foil; it is enough to degrease the surface with ethanol. After nickel plating, the nickel coating applied on both sides of the foil is the same, that is, the initial structure of the foil does not affect the morphology of the coating. Since there is no difference on which side (matte or glossy) of foil the nickel plating is carried out, you can protect the polymer mask on either side, differences in the morphology of the coatings are observed only with varying process durations.
Figure 5. Micrographs of the nickel plated surface, samples 5000(a) and 5001(b), processing time 20 and 40 min respectively.

Figure 5 shows the surface of samples 5000 and 5001. It can be seen that when the process time increases, a noticeable enlargement of the nickel globules size occurs.

The surface of the obtained coatings was analyzed using SEM Hitachi TM3000 microscope (back-reflected electron mode).

Figure 6. Micrographs of the nickel plated (active) surface, samples 5009(a) and 5010(b).

The figure 6 shows, that on one-sided (protected with a polymer mask) samples 5009 and 5010, the required surface microstructure was obtained. The globule size is about 2-10 microns in diameter, which corresponds to the optimal [12]. It can be seen that with increasing time, the coating becomes denser and has fewer pores.

Further, in order to increase the coating area, microperforation was previously applied to the surface of the foil with a laser (the structure is shown on figure 3), and the back side was covered with a polymer mask (samples 5030 and 5031). On the sample 5030 surface (figure 7 a, b), it is noticeable that nickel globules began to form primarily at the edges of the perforations. Respectively, we see some ordered structure, the surface area of which is much larger compared to flat (figure 6). Nickel globules adhere to the foil very well; no delamination was observed.

However, with increasing time (sample No.5030, figure 7 c, d), the globules increase significantly and reach a size of 30 μm, and the previously obtained structure is lost and flattened.
Thus, we can conclude that the optimal coating is on sample No.5030. From the side of the polymer mask, no deposited nickel globules or films were found. The surface of the mask is quite flat, but there were some scuffs.

The structure of the polymer mask was maintained at a temperature of 98°C and a processing time of 20-40 minutes, no delamination occurred.

6. Results and discussion
The micrographs shows that the obtained surface microstructure is quite gauffer. The diameter of the nickel globules is about 2-10 microns in diameter, which is optimal.

The proposed nickel plating process is simple and easily reproducible. Parameters of the obtained beta sources can be quite simply set by the processing time.

If, nevertheless, the quality of the obtained sources does not meet the requirements, it is quite simple to restore nickel to the form of the initial electrolyte by dissolving the base in alkali. On the mask side and reaction vessel, nickel globules are completely absent.

The described above methods for increasing the area of the radiation source can be combined -- one can create a microrelief with a laser, then micro-corrugate on the rollers, mask the reverse side and then precipitate the Ni63 isotope.

![Figure 7. Micrographs of the nickel plated (active) surface of perforated foil, samples 5030(a,b) and 5031(c,d).](image-url)
Aluminium base foil is slightly curved during microcorrugation, less after rolling than after laser processing. A flat sample takes the form of a screw, as can be seen in the microphoto 3 and 4 - the image is rather difficult to focus. Perhaps this is because the filling of the sample with dots occurs sequentially, the laser passes from one edge to the other, and deformations accumulate cumulatively.

It is qualitatively clear that the more prominent the surface of the radiation source, the larger its area and a larger flow of beta particles goes to the betavoltaic converter. Since the reverse current of the converter p-i-n junction does not depend on the magnitude of the irradiation flux, the specific characteristics of the betavoltaic power source are thus increased.

However, it is very difficult to prevent an air gap between the corrugated uneven source and the betavoltaic converter. Therefore, an additional analysis of the influence of the magnitude of this gap on the flow of beta particles is necessary, as well as the search for the optimal shape of the radiating surface.

Acknowledgements
Research is performed with financial support from Russian Federal Targeting Program "Research and development for priority targets of Russian scientific-technological complex development years 2014-2020”, in accordance with the agreement 14.577.21.0117, unique identifier RFMEFI57714X0117. Micrographs were obtained with equipment of the Cooperative Research Center of Krasnoyarsk Science Center of the Siberian Branch of the Russian Academy of Sciences.

References
[1] Zelenkov P V, Sidorov V G, Lelekov E T, Khoroshko A Y, Bogdanov S V and Lelekov A T 2016 IOP Conference Series: Materials Science and Engineering 122 012036
[2] Chen H, Jiang L and Chen X 2011 J. of Physics D: Applied Physics 44 215303
[3] Bormashov V, Sergey T, Volkov A, Tarelkin S, Korostylev E, Golovanov F, Kuznetsov M, Teteruk D, Kornilov N, Terentiev S, Buga S and Blank V 2015 Phys. Status Solidi A 212 2539–2547
[4] Rahmani F and Khosravinia H 2016 Radiation Physics and Chemistry 125
[5] Davydov A, Fyodorov Y, Kiselev D and AV P 2016 J. Nano- Electron. Phys. 8 03049
[6] Munson C, Gaimard Q, Merghem K, Sundaram S, Rogers D, Sanoit J, Voss P, Ramdane A, Salvestrini J and Ougazzaden A 2017 Journal of Physics D: Applied Physics 51
[7] Yunpeng L, Xiao G, Zhangang J and Tang X 2018 Applied radiation and isotopes 135 47--56
[8] Gui G, Zhang K, Blanchard J and Ma Z 2015 Applied Radiation and Isotopes 107
[9] Uhm Y, Choi B, Kim J, Jeong D–H and Son K 2016 Nuclear Engineering and Technology 48
[10] Bulyarskiy S, Abanin I and Lakalin A 2018 Characterization and Application Nanomaterials 1
[11] Liu Y M, Lu J B, Li X Y, Xu X, He R and Wang H D 2018 Nuclear Science and Techniques 29
[12] Kovalev I V, Sidorov V G, Zelenkov P V, Khoroshko A Y and Lelekov A T 2015 IOP Conference Series: Materials Science and Engineering 94 012024