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PROBABILITY THEORY OF DEGRADATION OF THERMOELECTRTIC ENERGY CONVERTERS AND ITS USE TO DETERMINE THE RELIABILITY OF THERMOELECTRIC MATERIALS

A probabilistic theory of degradation of thermoelectric energy converters has been developed, which describes such stages of their life cycle as the run-in period, which is described by the Weibull function, the period of stable operation, during which the failure rate is not necessarily constant, and the period of mass failures. To correctly describe these stages, the theory introduced the limit resource of a thermoelectric energy converter, which is consumed over time according to a nonlinear law and is precisely determined by the limit capabilities of thermoelectric and other materials, as well as contact structures. But this limit resource is a generalized integral characteristic of the limit resource capabilities of all materials used to create a thermoelectric energy converter and cannot be unambiguously "distributed" between them. After its complete consumption, there is a complete loss of performance of the thermoelectric energy converter. The parameters of the theory are determined by the least squares method based on processing the results of life tests. By combining the results obtained with a diffusion-nonmonotonic distribution of failure times, the parameters of which are also determined by the least squares method, it is possible to obtain such integral indicators of the reliability of materials as the average limit resource, 95 % limit resource, the minimum achievable equivalent failure rate and relative errors, in this case – with a confidence probability of 0.95.). Bibl. 7, Fig. 2, Tabl. 2.

Key words: probability theory of degradation of thermoelectric energy converters; limit resource of thermoelectric energy converter as the average limit resource of thermoelectric materials; 95 % limit resource of thermoelectric materials; minimum achievable equivalent failure rate, relative errors in their determination

Introduction

The theory of degradation of thermoelectric energy converters outlined in this article, suitable for determining their reliability indicators, can be exclusively probabilistic, since justified procedures and techniques for introducing random factors into a purely deterministic description of physical phenomena and processes that determine failures do not exist today [1]. The purpose of the article is the development of this theory and its application to the calculation of reliability indicators of thermoelectric materials and thermoelectric energy converters.

The simplest form of such a theory is the currently widely used linear theory of relative

parameter degradation, which is widely used in microelectronics [2].

Description and mathematical form of the theory

In its most general form, the developed generalized probabilistic theory of degradation of thermoelectric energy converters takes into account the following aspects of the physics of their failures.

- 1. There is such a threshold time τ , prior to which failures do not occur.
- 2. Gross technological defects in the manufacture of thermoelectric energy converters are rejected the fastest, that is, there is a "run-in period", during which degradation of the thermoelectric energy converter occurs according to Weibull's law.
- 3. There is a limit resource of a thermoelectric energy converter, which is consumed over time according to a nonlinear law.
- 4. Therefore, the mathematical form of the developed theory is as follows:

$$V(t) = V_0 \exp\left(-\frac{\left(\frac{t-\tau}{t_0}\right)^{\alpha}}{\gamma \left(1-\frac{t}{t_0}\right)^{\beta}}\right)$$
(1)

where V(t) is time-dependent parameter – suitability criterion of thermoelectric energy converter (most often output power or efficiency), t_0 is limit resource, α is parameter of Weibull's – distribution shape, γ is scale parameter β is indicator of nonlinearity of limit resource consumption, τ is threshold time.

However, in a partial case $-\tau = 0$ $t_0 \rightarrow \infty$ we will get the simplest partial modification of the developed theory, which is based on Weibull's law, namely:

$$V(t) = V_0 \exp\left(-\left(\frac{t}{t_s}\right)^{\alpha}\right)$$
(2)

where

$$t_s = t_0 \gamma^{1/\alpha} \tag{3}$$

This is the simplest modification of the developed theory which turns into a linear one at $\alpha = 1$ and $t \ll t_s$.

This is the simplest modification of the developed theory, which does not take into account the presence of a finite limit resource of thermoelectric energy converters, and was used to predict the results of life tests of thermoelectric energy converters in the absence of their obvious failures when they lose 20 % and 90 % of the output power [3 - 5]. Based on the results of this forecasting, a function of the probability of failure-free operation was first built in tabular form for a selected

sample of thermoelectric energy converters relative to their loss of 20 % of the output power. And after that, the obtained data were smoothed by the least squares method, following which the most plausible estimates of the parameters of the diffusion-nonmonotonic law of failure times distribution were determined and then - reliability indicators and relative errors of their determination. This law was developed by the Institute of Mathematical Machine Problems of the National Academy of Sciences of Ukraine and standardized in the DSTU project 300495 "Reliability of equipment. Methods of estimating reliability indicators based on experimental data". Therefore, with the use of the simplest modification of the developed probabilistic theory of degradation of thermoelectric energy converters, the following indicators of their reliability and relative errors of their determination with a confidence probability of 0.99 were obtained: mean time between failures (MTBF) 11770 h with a relative error of 11.9 %, 95 % resource 9170 h with a relative error of 26.5 %. Therefore, with the use of the simplest modification of the developed probabilistic theory of degradation of thermoelectric energy converters, the following indicators of their reliability and relative errors of their determination with a confidence probability of 0.99 were obtained: mean time between failures (MTBF) 11770 h with a relative error of 11.9 %, 95 % resource 9170 h with a relative error 26.5 %. The equivalent failure rate constant was $\lambda = 8.172 \cdot 10^{-5} \text{ h}^{-1}$ with a relative error of 10.5 %.

At first glance, this failure rate may seem significant, but it should be taken into account that each of the tested thermoelectric energy converters consists of 127 series connected thermoelements. And from this it follows that the equivalent failure rate of one thermoelement in the mode of electrical energy generation is $6.435 \cdot 10^{-7}$ h⁻¹, which is approximately 3.1 times less than the minimum value given in [6], which is equal to $2 \cdot 10^{-6}$ h⁻¹

On the other hand, the calculation of the reliability indicators of thermoelectric energy converters relative to their loss of 90 % of power or efficiency was necessary because the initial modification of the developed generalized probabilistic theory of degradation of thermoelectric energy converters did not assume the presence of their limit resource. And among others, we were faced with the task of comparing the reliability of thermoelectric energy converters with different electrical connection circuits for thermoelements. And the formulation of such a problem itself is relevant and meaningful when, in the case of a purely series circuit for connection of thermoelements, loss of integrity of at least one thermoelectric leg is possible. In this case, if we do not consider options for shunting or special protection of thermoelectric legs or transition from a purely series circuit of their connection to a parallel, series-in-parallel or parallel-in-series circuit, then it turns out that the loss of the integrity of at least one leg leads to a complete failure of the thermoelectric energy converter as a whole. In this case, the breakdown of the electrical circuit of a leg can be either instantaneous and caused by its destruction as a whole due to the action of thermomechanical stresses caused by cyclic temperature effects or purely mechanical stresses caused by accelerations or shock loads. The specific values of these stresses and their distribution in the bulk of the thermoelectric leg are determined by one or another method of material resistance within the framework of the corresponding physical models. After that, with the use of certain modifications of the Weibull approach, the established stress distribution is associated with the probability of destruction of the thermoelectric leg. Further, it is assumed that all thermoelectric legs, without exception, which are part of the thermoelectric energy converter, are considered to be the same and to fail with equal probability. Without such an assumption, calculations are dramatically complicated.

But the destruction of the electrical circuit of one or more legs can occur gradually during the functioning of the thermoelectric energy converter in the operating mode. The main factor of such destruction can be, for example, the gradual accumulation of cavities and cracks in the transient contact layer due to the formation of intermetallic compounds. In particular, such processes can determine the limit resource of the thermoelectric energy converter, which appears in formula (1).

Determination of theory parameters

The parameters of the theory are determined for each of the thermoelectric energy converters subjected to life tests using the least squares method based on experimental data on the time change in the output power of each of them.

Determination of the predicted time of failures of thermoelectric energy converters

The advantage of the developed probabilistic theory of degradation of thermoelectric energy converters is that given one or another sign of failure, determined by the scientific and technical documentation for products or by agreement with the customer, we can determine the standardized reliability indicators of thermoelectric energy converters even in the absence of their obvious failures during operation. In this case, we considered a loss of 20 % of the initial power of each of the tested thermoelectric energy converters as a failure. Therefore, determining the failure time of each module from formula (1) and ordering the obtained times in ascending order, we obtained the following table of the probability of failure-free operation of the tested thermoelectric energy converters:

<u>Table 1</u>

<i>t</i> , <i>h</i>	9390	10020	11160	11250	15600
P(t)	0.8	0.6	0.4	0.2	0

Table of the probability of failure-free operation of thermoelectric energy converters,when a loss of 20 % of their output power is considered a failure

Reliability models for determining reliability indicators of thermoelectric materials and energy converters

«"Diffusion-nonmonotonic" reliability model for determining standardized reliability indicators of thermoelectric energy converters

Then, based on the diffusion-nonmonotonic distribution of failure times, the most plausible estimates whose parameters are determined by processing table (1) by the least squares method, the following estimates of the standardized reliability indicators of the tested energy converters with respect to a 20 % loss of generated power are obtained: mean time between failures (MTBF) 11480 h with a relative error of 15.3 % at a confidence probability of 0.95, 95 % resource 7702 h with a relative error of 33.5 % at the same confidence probability and an equivalent constant failure rate $\lambda = 7.716 \cdot 10^{-5} \text{ h}^{-1}$ with relative error of 15.1 % for the same confidence probability. Hence, the equivalent constant failure rate of one thermoelement is equal to $6.03 \cdot 10^{-7} \text{ h}^{-1}$, which is approximately 3 times greater than the experimental value given in [6].

Determination of the limit resource of thermoelectric energy converters and integral indicators of the reliability of thermoelectric materials

Now we will consider the complete loss of functionality of the module as a sign of failure. In this case, we will get the following table of the probability of trouble-free operation:

Table 2

Table of the probability of failure-free operation of thermoelectric energy converters for the case when the failure is considered to be a drop in the output power to zero

<i>t</i> , <i>h</i>	$2.624 \cdot 10^{6}$	$2.934 \cdot 10^{6}$	$2.992 \cdot 10^{6}$	$3.335 \cdot 10^{6}$
P(t)	0.75	0.5	0.25	0

And in this case, based on the diffusion-nonmonotonic distribution of failure times, the most plausible estimates of whose parameters are determined by the least squares method, the following estimates of the standardized reliability indicators of the tested energy converters relative to complete failure are obtained: average limit resource (MTBF) $2.91 \cdot 10^6$ h with a relative error of 5.3 % at a confidence probability of 0.95, 95 %, a limit resource of $2.61 \cdot 10^6$ h with a relative error of 12.9 % at the same trust probability and the minimum achievable failure rate $\lambda = 3.38 \cdot 10^{-6}$ h⁻¹ with a relative error of 15.1 % for the same confidence probability. Hence, the equivalent constant failure rate of one thermoelement is equal to $2.64 \cdot 10^{-8}$ h⁻¹

But failures during a significant period of operation which consist in the complete loss of efficiency of thermoelectric converters and resource indicators determined on their basis can be interpreted as indicators of resource stability of least stable materials, or integral indicators of resource stability of materials that are part of a thermoelectric energy converter. But based only on the results of life tests, it is impossible to "separate" the mentioned indicators by individual materials. That is why they are called integral.

However, such an interpretation is at least qualitatively consistent with the results of work [7], which shows that, for example, the processes of diffusion of nickel into the thermoelectric material do not lead to a significant change in the efficiency of thermoelements in the mode of generating electrical energy even for 50 years, i.e. 438300 h, if they are not accompanied by the formation of intermetallic compounds.

It is also consistent with the results of work [8], which shows that if thermoelectric legs based on bismuth telluride are protected so that the flow of sublimated tellurium atoms through their surface does not exceed $7.5 \cdot 10^{15}$ m⁻²s⁻¹, then the complete depletion of a thermoelectric leg with a length of 1.5 mm based on bismuth telluride doped with an excess of tellurium will occur no earlier than in 100 years, i.e. 876,600 hours.

In this way, it is possible to introduce the following integral indicators of resource stability of materials that are part of thermoelectric energy converters: the average limit resource, which is equal to $2.91 \cdot 10^6$ h with a relative error of 5.3 % with a confidence probability of 0.95, 95 %, the limit resource, which is equal to $2.61 \cdot 10^6$ h with a relative error of 12.9% for the same confidence probability and the equivalent minimally achievable constant failure rate, which is equal to $\lambda = 3.38 \cdot 10^{-6} \text{ h}^{-1}$ with a relative error of 15.1 % for the same confidence probability.

The results of these calculations are illustrated in Figs.1, 2

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Fig. 2. Dependences of the probability of realization of a certain limit resource of thermoelectric energy converters on the value of this resource: 1 – the most probable in accordance with the diffusion-monotonic law of the distribution of failure time,
2, 3 – limit with a confidence probability of 0.95, triangles– the results of predicting the limit resource according to the probabilistic theory of degradation

Conclusions and recommendations

- 1. A generalized probabilistic theory of degradation of thermoelectric energy converters has been developed, which covers such periods of their operation as the run-in period, the period of stable operation, and the period of mass failures.
- 2. Run-in within the framework of the developed theory is described by Weibull's law.
- 3. The theory explicitly takes into account the limit resource of thermoelectric energy converters, which is consumed over time according to a non-linear law and is determined by the resource capabilities of the least resource-resistant materials.
- 4. The theory also predicts the existence of a threshold time prior to which failures do not occur.
- 5. The developed theory, being combined with the diffusion-nonmonotonic law of failure time distribution, allows, based on the results of life tests with acceptable accuracy and an acceptable confidence level, to calculate reliability indicators of thermoelectric energy converters even with a small volume of the test sample and even in the case when there are no obvious failures during testing.
- 6. As a result of applying the developed theory to processing the results of resource tests of thermoelectric energy converters, the following indicators of their reliability were obtained:
 average run-in with preservation of 80 % of output power (MTBF) 11.480 h with a relative error of 15.3 % at a confidence level of 0.95; 95 % resource of preservation of 80 % of output power 7702 h with a relative error of 33.5 % for the same confidence probability; and the equivalent constant failure rate λ = 7.716 · 10-5 h-1 with a relative error of 15.1 % for the same confidence probability. Hence, the equivalent constant failure rate of one thermoelement is

equal to $6.03 \cdot 10^{-7}$ h.⁻¹;

- average run-in to complete failure (MTBF) or the average limit resource $2.91 \cdot 10^6$ h with a relative error of 5.3 % at a confidence probability of 0.95, a 95 % resource of $2.57 \cdot 10^6$ h with a relative error of 12.9 % at the same confidence probability and the minimum achievable failure rate $\lambda = 3.38 \cdot 10^{-6}$ h⁻¹ with a relative error of 15.1 % for the same confidence probability. Hence, the equivalent constant failure rate of one thermoelement is equal to $2.64 \cdot 10^{-8}$ h⁻¹.

7. The obtained results can be used for the research of accelerated tests.

References

- 1. Anatychuk L. I., Luste O. (2017). Model studies of degradation mechanisms of thermoelectric materials and contact structures. *J.Thermoelectricity*, 4, 62 88.
- Gorskyi P. V. (2022). Peculiarities of determining reliability indicators of thermoelectric generator modules based on experimental data. *Technology and Design in Electronic Equipment*, 1-3, 50 – 56. http://dx.doi.org/10.15222/TKEA2022.1-3.50.
- 3. Gorskyi P. V. (2022). Comparison of the reliability of thermoelectric generator modules with different circuits of electric connection of thermoelements. *Technology and Design in Electronic Equipment*, 1 3, 59 64. http://dx.doi.org/10.15222/TKEA2022.4-6.59.
- Gorskyi P. V. Peculiarities of determining reliability indicators of thermoelectric generator modules. In: Proceedings of the XXII International Scientific and Practical Conference of the ISPC CIET-XXII Odesa – 2022, May 23 – 27. – P. 38 – 39.
- 5. G. K. Kotyrlo (1980). Raschiot i konstruirovaniie termoelektricheskikh generatorov i teplovykh nasosov. Spravochnik. [Calculation and design of thermoelectric generators and heat pumps. Handbook]. Kyiv: Naukova dumka.

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- 6. Gorskyi P. V. (2023). Do thermoelectric generator modules degrade due to nickel diffusion. *Technology and Design in Electronic Equipment*, 3-3-4, 59-64. http://dx.doi.org/10.15222/TKEA2023.3-4-.59.
- Sublimation of volatile component as a possible mechanism of thermoelectric material degradation. (2022). *Physics and Chemistry of the Solid State*, 23, 204–209. DOI:1015330/pcss23.2.204-209

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ІМОВІРНІСНА ТЕОРІЯ ДЕГРАДАЦІЇ ТЕРМОЕЛЕКТРИЧНИХ ПЕРЕТВОРЮВАЧІВ ЕНЕРГІЇ ТА ЇЇ ВИКОРИСТАННЯ ДЛЯ ВИЗНАЧЕННЯ НАДІЙНОСТІ ТЕРМОЕЛЕКТРИЧНИХ МАТЕРІАЛІВ

Розроблено імовірнісну теорію деградації термоелектричних перетворювачів енергії яка описує такі етапи їх життєвого циклу, як період припрацювання, який описується функцією Вейбула, період стабільного функціонування, на якому інтенсивність відмов не обов'язково є сталою та період масових відмов. Для коректного опису вказаних етапів у теорію введено граничний ресурс термоелектричного перетворювача енергії,який витрачається з часом за нелінійним законом і якраз і визначається граничними можливостями термоелектричних та інших матеріалів а також контактних структур. Але цей граничний ресурс є узагальненою інтегральною характеристикою граничних ресурсних можливостей всіх матеріалів, використаних при створенні термоелектричного перетворювача енергії і не може бути однозначно «розподілений» між ними. Після його повної витрати настає повна втрата праиездатності термоелектричного перетворювача енергії. Параметри теорії визначаються методом найменших квадратів на основі обробки результатів ресурсних випробувань. Об'єднуючи отримані результати з дифіузійнонемонотонним розподілом часу відмов, параметри якого також визначаються методом найменших квадратів, можна отримати такі інтегральні показники надійності матеріалів, як середній граничний ресурс, 95 % граничний ресурс мінімальну досяжну еквівалентну інтенсивність відмов та відносні похибки їх визначення (у даному випадку – за довірчої ймовірності 0.95). Бібл. 7, рис. 2, табл. 2.

Ключові слова: ймовірнісна теорія деградації термоелектричних перетворювачів енергії, Граничний ресурс термоелектричного перетворювача енергії, як середній граничний ресурс термоелектричних матеріалів, 95 % граничний ресурс термоелектричних матеріалів, мінімальна досяжна еквівалентна інтенсивність відмов, відносні похибки їх визначення.

References

- 1. Anatychuk L.I., Luste O. (2017). Model studies of degradation mechanisms of thermoelectric materials and contact structures. *J.Thermoelectricity*, 4, 62 88.
- Gorskyi P.V. (2022). Peculiarities of determining reliability indicators of thermoelectric generator modules based on experimental data. *Technology and Design in Electronic Equipment*, 1-3, 50 – 56. http://dx.doi.org/10.15222/TKEA2022.1-3.50.
- 3. Gorskyi P.V. (2022). Comparison of the reliability of thermoelectric generator modules with different circuits of electric connection of thermoelements. *Technology and Design in Electronic Equipment*, 1 3, 59 64. http://dx.doi.org/10.15222/TKEA2022.4-6.59.
- Gorskyi P.V. Peculiarities of determining reliability indicators of thermoelectric generator modules. In: Proceedings of the XXII International Scientific and Practical Conference of the ISPC CIET-XXII Odesa – 2022, May 23 – 27. – P. 38 – 39.
- 5. G.K. Kotyrlo (1980). Raschiot i konstruirovaniie termoelektricheskikh generatorov i teplovykh nasosov. Spravochnik. [Calculation and design of thermoelectric generators and heat pumps. Handbook]. Kyiv: Naukova dumka.
- 6. Gorskyi P.V. (2023). Do thermoelectric generator modules degrade due to nickel diffusion. *Technology and Design in Electronic Equipment*, 3-3-4, 59-64. http://dx.doi.org/10.15222/TKEA2023.3-4-.59.
- 7. Sublimation of volatile component as a possible mechanism of thermoelectric material degradation. (2022). *Physics and Chemistry of the Solid State*, 23, 204–209. DOI:1015330/pcss23.2.204-209

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