

# Diffusion Protection of Thermoelectric Cooler Junctions as a Means of Increasing its Reliability

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## Abstract

Experimental study of the influence of on-junctions metallization thickness on the stability of thermoelectric cooler (TEC) parameters under high temperature conditions is undertaken. Mechanical properties of the contacts are studied at various anti-diffusion layer thicknesses. The results obtained are used for developing TECs compatible with electro-optic elements on the factor of reliability.

## Introduction

The reliability and performance of a TEC, as well as those for any other multi-element device, depend substantially on the quality of thermoelement junctions. That is why TE legs connection is considered as the most important process in the TEC manufacturing. The key point of the process is the creation of protective metal plating onto the contacts of thermoelectric pellets with subsequent connection by soldering.

The metal coating on the contacts should meet a number of requirements. These are acceptably low contact resistance, high mechanical strength of the soldered joints, diffusion protection of TE legs resulting in maximum TEC reliability and long operating life. The problem of TECs reliability, when different methods of connection are used, have been studied by many authors [1-5]. For the bismuth telluride and its alloys, the contacts with sufficiently low electric resistance and good anti-diffusion properties have been obtained by applying nickel coating over the TE legs contact surfaces. In [2,4,5], it was mentioned that the diffusion of the solder components (for instance, tin) into a thermoelectric material is one of the major mechanisms of degradation which causes the failure of a cooler. That is why the creation of a reliable diffusion barrier on TE leg contacts is the most important step in the TECs technology.

It is evident that the anti-diffusion properties of the metal coating depend on the deposited layer thickness. The correct information in this field would greatly contribute to the reliability of thermoelectric devices. However, currently there are no experimental data on the dependence of degradation processes in a thermoelectric leg on the thickness of metal layers on its contacts. Two probable reasons can be an explanation of this fact: insufficient amount of systematic studies in this field and, probably, the routine of the TECs manufacturers, aimed to protection of their technological knowledge.

The other associated problem is to ensure contact mechanical strength at the Ni-Bi<sub>2</sub>Te<sub>3</sub> interface [4-8]. The dependence of the metal layer adhesion on its thickness has not been virtually considered in the literature. An exception is the paper [6], which contains experimental data on adhesion of the nickel layers of various thicknesses towards the thermoelements, based on extruded semiconducting materials. The measured breaking strength was rather high,

though the overall strength of contact is reported to decrease dramatically (more than by factor of two) as the Ni layer thickness increases from 2 to 10 μm. As the data amount is limited, the problem needs to be studied more thoroughly.

In this paper the determination of the optimum Ni coating thickness which provides reliable anti-diffusion TE leg protection coupled with good adhesion is undertaken. The results of experimental study of the influence of metal layers thickness on a TEC parameters stability under high temperature conditions are presented. It is shown that the improvement of contact quality is an efficient way of a TEC reliability enhancement. The mechanical properties of the contacts have been studied at various anti-diffusion layer thicknesses. The results obtained were used when developing TECs which are compatible with the elements of the optoelectronic systems on the factor of reliability.

## 1. Choice of the anti-diffusion layer thickness

The processes of ageing and thermo-diffusion in the thermoelectric coolers have been studied to determine the appropriate thickness of the nickel coating. The high-temperature storage test was used in this study as being the most indicative one for identification of a TEC degradation through the diffusion of solder components into the thermoelectric branch.

**Experimental samples.** The Thermion module 1MC06-018-10 containing 36 TE legs 1 mm long with the cross-section of 0.6x0.6 mm was chosen for high temperature tests. The reason for such choice is the fact that the coolers of this type are widely used in telecommunication systems for thermal management of optoelectronic elements. Five groups of the said coolers have been manufactured, each one with different thickness of the Ni coating (Table 1). Each group contained 5 identical samples. The Ni layers were produced using electroless Ni deposition. The layer thickness was measured by optical method with the use of metallurgical microscope MMR-2R. The coolers were assembled with the 183°C 60%Sn40%Pb solder. In all the samples, the extruded TE materials were used supplied by the NORD, Moscow.

**Method and result of the researchs.** Each group of the TECs was inserted into an open glass ampoule and loaded in the thermostatic chamber.

**Table 1.** The range of nickel layer thickness

Group №	Ni layer thikness, $\delta$ (μm)
1	1.6
2	2.4
3	2.8
4	3.2
5	3.7

The test was conducted at the constant temperature of 135°C in the open air. It is worth to note that these conditions exceed the Telcordia GR-468-CORE requirements [9], which define the test as a high-temperature exposure under the inert gas or vacuum. The total test duration exceeded 14,000 hours. The TECs were extracted periodically to measure their electric resistance  $R$  and figure of merit  $Z$ . The Harman's method was used throughout the experiments instead  $\Delta T_{\max}$  measurement. Possibility and expediency of such substitution is based on interdependency of these parameters and substantial reduction of the tests duration. Fig. 1 and 2 show the time-dependence of the normalized averaged  $\bar{R}$  and  $\bar{Z}$  values for each group of TECs under study.

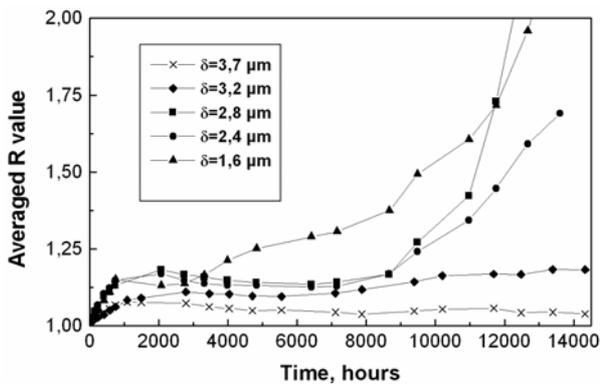


Fig.1 Averaged values of electrical resistance for different TEC groups. High temperature storage, 135°C, open air. Data are normalized at averaged initial values.

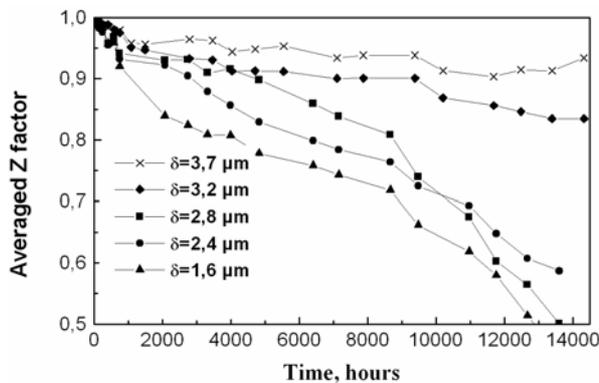


Fig.2 Averaged values of Z factor for different TEC groups. High temperature storage, 135°C, open air. Data are normalized at averaged initial values.

It is seen clearly that the coolers in groups 1, 2, and 3, having Ni layers thickness under 3  $\mu\text{m}$ , suffered from  $R$  and  $Z$  reduction within first 500-600 hours of high-temperature storage. In this period, the resistance increased by 20-25%, while the quality parameter  $Z$  decreased by 10%, indicating catastrophic degradation of the modules in these groups. Later on, the intensive degradation of the TECs persisted, what proves the insufficient diffusion protection of the joints caused by inadequate thickness of the Ni coating.

Something better results were observed in Group 4, where Ni layer thickness was 3.2  $\mu\text{m}$ . Though the resistance of the modules was increasing in this group too, the

degradation process was not catastrophic. Within the time range from 2,000 to 9,000 hours, the stabilization of the  $R$  and  $Z$  parameters was observed, however, after 9,000 hours of exposure at 135°C degradation rate increased over again.

The fundamental enhancement of the  $R$  and  $Z$  stability was obtained in the group 5, where the nickel layer thickness was of 3.7  $\mu\text{m}$ . The coolers showed the stable characteristics with practically unchanging  $R$ , complying with the Telcordia GR-468-CORE requirements for the case with inert gas or under vacuum.

It is seen also that the approaching to the thickness of 4.0  $\mu\text{m}$  does not exhaust the potential for TEC perfection, and, consequently, it would be necessary to proceed the researches with thicker layers coupled with experimental definition of their adhesion to the  $\text{Bi}_2\text{Te}_3$ -based TE materials.

## 2. Mechanical Tests

In order to assess the adhesion properties of the nickel coating produced accordingly to Termion's technology, the authors have conducted the ultimate tensile strength tests. For this purpose, four groups of P-type pellets and four groups of N-type pellets were manufactured with the thicknesses of the nickel coating of 3.7, 4.4, 5.3, and 5.8  $\mu\text{m}$ . Each group comprised three identical samples with the height of 1.2 mm and cross-section of 3.2x3.2 mm. Total tested are 12 samples for each type of conductivity.



Fig. 3. Tensile machine for determination of Ni layer adhesion strength.

The ultimate contact tensile strength was measured using the special screw-loading machine with standard dynamometer DOSM-3-0.05 (Fig. 3). Prior to testing, short metal rods with the cross section of 3.2x3.2 mm were soldered to the contact surfaces of the samples. The tensile stress load was applied by two steel strings, attached to the middle parts of the rods via swivel joints, which excluded lateral and misalignment loads during testing. The tensile load was created by screw mechanism, providing longitudinal tension of the strings. The ultimate tensile stress was measured by the dynamometer at the moment of sample destruction. The test results are shown in Table 2

In contrast to [6], in our experiments we did not recorded any reduction of junctions strength when increasing Ni layer thickness in the range from 3 to 6 microns. This

gives prospects for farther Ni layer thickening with simultaneous perfection of its anti-diffusion properties.

It is worth to note that in the prevailing number of experiments the samples destruction took place in the bulk TE material without cleaving of the junction itself (a typical image of a fracture surfaces is shown at the Fig.4). This means that the real contact strength is not determined in these experiments, we can only claim that the adhesion strength of Ni contact is normally stronger than TE material. It should be noted that some samples showed tensile strength up to 38 MPa for P-type and more than 45 MPa for N-type material depending on the own pellet strength.

**Table 2.** Result of ultimate tensile strength tests

Type	Sample No.	Ni layer thickness ( $\mu\text{m}$ )			
		3.7	4.4	5.3	5.8
P	1	25.0	29.0	-	26.2
	2	24.0	23.0	21.0	21.4
	3	25.0	24.5	29.0	26.7
Averaged value		24.7	25.5	25.0	24.8
N	1	35.3	32.8	33.0	35.0
	2	35.3	34.0	31.8	35.3
	3	29.7	28.0	36.5	28.3
Averaged value		33.4	31.6	33.8	32.9



Fig. 4. The typical image of the TE pellet destruction.

### 3. Application

The results of this study were used in developing miniature TEC, destined for cooling X-ray detectors inside the "mini-butterfly" electronic header. The general view of the microcooler is shown at the Fig. 5. The cooler comprises 22 thermoelectric pellets 0.8 mm high with the cross-section of 0.4x0.4 mm and two 2.4x6.4x0.3 mm ceramic substrates. The full set of the tests has been carried out including mechanical and long-term thermal and electric impacts. The total 73 TECs have been tested, what provides statistical confidence of the results obtained.

The conditions and results of the environmental and mechanical tests are shown in Table 3-4 and at Fig. 6-9. As it is seen from Figures and Tables, in all the cases the results obtained meet the reliability criteria assigned for electronic system components [9].



Fig. 5. Thermoelectric micro-cooler 1MC(L)04-011-08.

The changes in  $R$  and  $Z$  parameters lay within the permissible ranges and no TEC failure was revealed, what can serve as a sufficient evidence of high reliability of the developed micro-coolers.

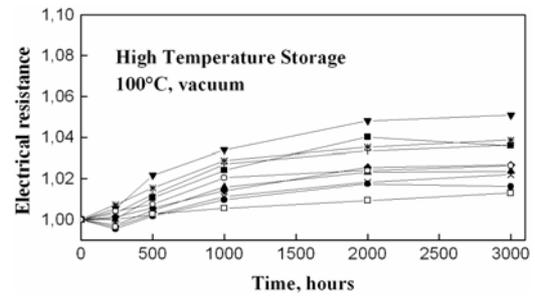


Fig. 6 Time dependence of the TECs electrical resistance normalized at its initial value. High temperature storage, 100°C, vacuum.

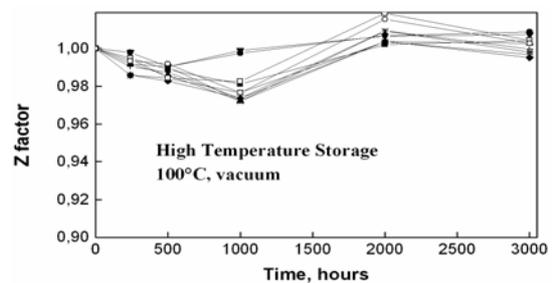


Fig. 7 Time dependence of the TECs figure of merit normalized at its initial value. High temperature storage, 100°C, vacuum.

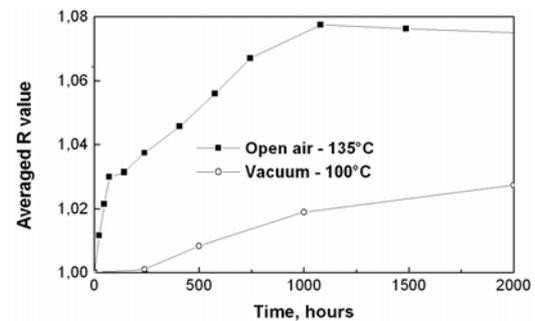


Fig. 8. Time dependence of averaged values of electrical resistance under different conditions of high temperature storage. Data are normalized at averaged initial values.

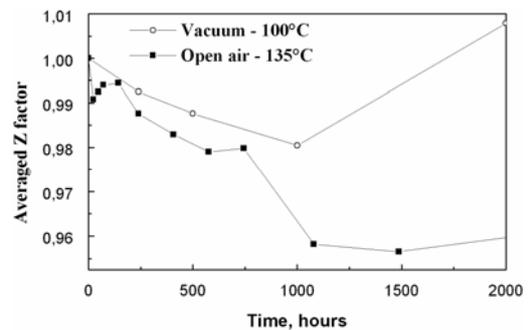


Fig.9. Time dependence of averaged values of Z factor under different conditions of high temperature storage. Data are normalized at averaged initial values.

Table 3. Conditions and results of environmental tests

Test	Test Conditions	Maximum Change
Power Cycling	Heat sink at +70°C, open air, $I=I_{max}$ , 1.5 min on / 4.5 min off, 5000 cycles, 10 samples	$\Delta R/R = 3,1 \%$ $\Delta Z/Z = -1,5\%$
Temperature Cycling	Temperature range from -47 to +88°C, 500 cycles, vacuum	$\Delta R/R = -0,35 \%$ $\Delta Z/Z = 2,65 \%$
Thermal Shock	Temperature range from 0 to 100°C (water ice/boiling water), 20 cycles, 10 samples	$\Delta R/R = 2,9 \%$
High Temperature Storage	Ambient temperature: 100°C, vacuum, 2000 hours, 10 samples	$\Delta R/R = 4,8 \%$ $\Delta Z/Z = 1,9 \%$

Table 4. Conditions and results of mechanical tests

Test	Test Conditions	Maximum Change
Mechanical Shock	Acceleration -1500 g, puls duration - 0.5 ms, 5 shocks along x, y, z axes in both directions, 10 samples	$\Delta R/R = 2,01 \%$ $\Delta Z/Z = -2,44\%$
Random Vibration	Acceleration - 20 g, frequency range – 20-2000 Hz, 4 min/cycle, 4 cycles, axes x, y, z, 10 samples	$\Delta R/R = 0,35 \%$ $\Delta Z/Z = 2,03 \%$
Die Shear Strength	Bottom substrate glued to the fixed base, shear force applied to the top substrate, destruction force to be not less than 21,1 H [13], 10 samples	Actual Destruction Force: 29,6 < F < 45,1 (H)

Due to the absence of catastrophic degradation of TECs during environment tests, it is impossible to develop a statistical model to forecast the life duration of the TECs under study, this is because a sufficient number of failures is necessary for such model definition [8, 10, 11]. To solve this problem, it is advisable to use the results of accelerated tests under more severe conditions than those required by the current technical standards. Definite conclusions can be done, for instance, basing on the results of TECs high temperature storage under different environmental conditions. Fig. 8 and 9 show the comparison of the results of TECs high-temperature tests with the following conditions: 1) standard test: vacuum, temperature 100°C; 2) accelerated test: open air, temperature 135°C. It is seen that in the case 2, the change in the TEC resistance is considerably higher than that for the case 1. This discrepancy can be used to forecast the life duration of the TECs under standard conditions, basing on the results of accelerated tests.

## 5. Conclusion

Efficient diffusion protection of the TEC junctions is the most important means to considerably enhance TEC reliability and life duration. The properly carried out process of electroless Ni deposition provides low contact resistance, high mechanical strength of the soldered joints and diffusion protection of TE legs resulting in maximum TEC reliability.

It is shown that the adhesion strength of the Ni layer to the Bi<sub>2</sub>Te<sub>3</sub> alloy exceeds normally the strength of a bulk TE material and can reach 40-45 MPa.

The results obtained are used for developing TECs compatible with electro-optic components in terms of reliability.

## References

1. Click, P.Jr., and Marlow R, "Reliability and Failure Modes of Thermoelectric Heat Pumps," *Proc. 2nd Intern. Conf. on Thermoelectrics.* – 1978, p. 115-120.
2. Thermoelectric Cooler Reliability Report, Marlow Industries, inc, Telecommunication Industry, 1992, 58 p.
3. Melcor Thermoelectric Cooler Reliability Report, Melcor Corporation, 2002, 36 p.
4. Redstall, R.M., and R. Studd, Reliability of Peltier Coolers in Fiber-Optic Laser Packages, in Thermoelectrics Handbook, (New York, London, Paris, 1995), pp. 641-645.
5. Ritzer Todd M., et al, "A Critical Evaluation of Today's Thermoelectric Modules," *Proc. 16<sup>th</sup> Intern. Conf. on Thermoelectrics*, 1997, pp. 619-623.
6. Vasilevskiy D., et al, "Mechanical Properties of the Interface between Nickel Contact and Extruded (Bi<sub>1-x</sub>Sb<sub>x</sub>)<sub>2</sub>(Te<sub>1-y</sub>Se<sub>y</sub>)<sub>3</sub> Thermoelectric Materials," *Proc. 25<sup>th</sup> Intern. Conf. on Thermoelectrics*, 2006, p. 666-669.
7. Zhenmao Liu, et al, "Reliability investigation of semiconductor coolers," *Proc. 16<sup>th</sup> Intern. Conf. On Thermoelectrics*, 1997, p. 708-710.
8. Semenyuk V.A., Antonenko A.V. "Issledovanie nadezhnosti termoelektricheskikh ohladitelej," *Refrigeration engineering and technology, № 2 (106) (2007)*, p. 17-24 (in Russian).
9. Reliability Assurance Requirements for Optoelectronic Devices. Telcordia GR-468-CORE. Issue 2, September 2004.
10. Anatychuk L.I., Luste O.J., "On the Reliability of Thermoelectric Cooling and Generator Modules," *Proc. 17<sup>th</sup> Intern. Conf. On Thermoelectrics*, 1998, pp. 101-104.
11. Bierschenk J., Gilley M., "Assessment of TEC Thermal and Reliability Requirements for Thermoelectrically Enhanced Heat Sinks for CPU Cooling Applications," *Proc. 25<sup>th</sup> Intern. Conf. On Thermoelectrics*, 2006. p. 254-259.
12. Ritzer T.M., "Quick Method for Determining the Reliability of a Thermoelectric Module via Pulse Testing," *Proc. 18<sup>th</sup> Intern. Conf. on Thermoelectrics*, 1999, pp. 432-435.
13. Department of Defense Test Method Standard Microcircuits. MIL-STD-883F, Method 2019.7, Die Shear Strength//AMS N/A, FSC 5962, June 2004, 97 p.