Experimental characterization of thermoelectric properties of thick film composites

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Abstract

This paper presents thermoelectric properties of thick-film composites in relation to their potential use as power microgenerators. Several different combinations of composites were used to create thermopiles. One track of each thermocouple was made of PdAg or Pt and was the reference track and the second one of the tested material. After preliminary tests five composites with low resistance and adequate Seebeck coefficient were chosen (Ag, Ag+RuO_2 and three kinds of RuO_2). We measured the Thermoelectric Force, E_T = f(ΔT) and internal resistance R_i = f(T) characteristics over the temperature range 293 to 493 K. PdAg/Ag thermocouples have nearly two orders of magnitude higher output electrical power than the others. The change in values of electrical parameters of thermopiles after long-term ageing processes was also investigated.

Key words

Thermoelectricity, thermocouple, thermopile, Seebeck coefficient, microgenerator, thick film

1. Introduction

A thermoelectric circuit consisting of two connected sections with each section being made of a different material is called a thermocouple. When hot and cold junctions are held at different temperatures, the thermoelectric power ET is generated. When two or more thermocouples are electrically connected in series and thermally in parallel a thermopile is formed. Under matching-load conditions, the maximum electrical output power generated by a thermocouple can be expressed in terms of the open circuit voltage, as:

$$P_{MAX} = \frac{E_T^{\ 2}}{4R_i}$$

where R_i is the internal electric resistance of a thermopile, E_T is the thermoelectric force ($E_T = n\cdot\alpha\cdot\Delta T$, where α - Seebeck coefficient, ΔT – temperature difference between hot and cold junction, n – number of thermocouples in thermopile).

To fabricate a thermoelectric generator with optimal parameters (high output thermoelectric power) it is important to pay attention to materials properties such as the Seebeck coefficient, thermal resistivity and electrical conductivity. Thermal resistivity of substrate is also important. All of these parameters can be easily determined, using experimental methods [1, 2]. Thermocouples can be used not only in measuring temperature, but also in measuring power generation [3], insolation, humidity and vacuum [4].

2. Test samples fabrication

Results presented in this paper are a continuation of our earlier work [3]. Several different combinations of composites were used to create thermopiles. After preliminary tests, five composites with low resistance and adequate Seebeck coefficient were chosen: Ag or Ag+RuO2-based conductive inks and three versions of low-resistive inks based on RuO2 – one specially prepared by ESL and two from inks delivered by Rzeszow University of Technology. The last two inks have different contents of conductive phase – 28% and 40% of volume.

The tracks (arms) were screen-printed on rectangular (25x30 mm2) alumina substrates using 325 mesh (PdAg and Pt) or 400 mesh (tested materials) stainless screens and cofired at 1073, 1123 or 1173 K. Masks used for screen-printing of reference tracks and tested tracks are shown in Figs. 1(a) and 1(b). Three thermopiles with different-width thermocouples were fabricated (0.3, 0.5 and 0.7 mm in width) on each single substrate. Each thermopile was 22 mm in length and consisted of four thermocouples. Example of a measured structure is shown in Figure 1 (c).

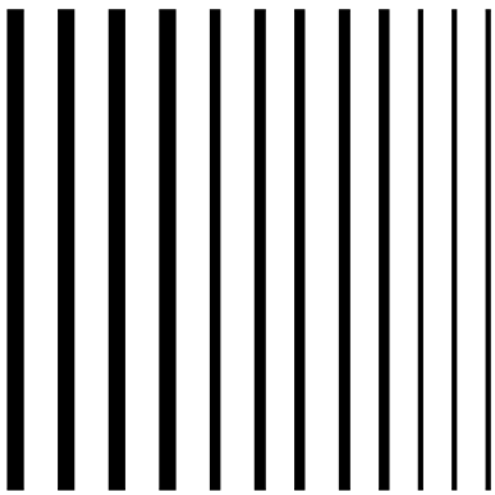


Fig. 1(a). Mask for Reference Tracks

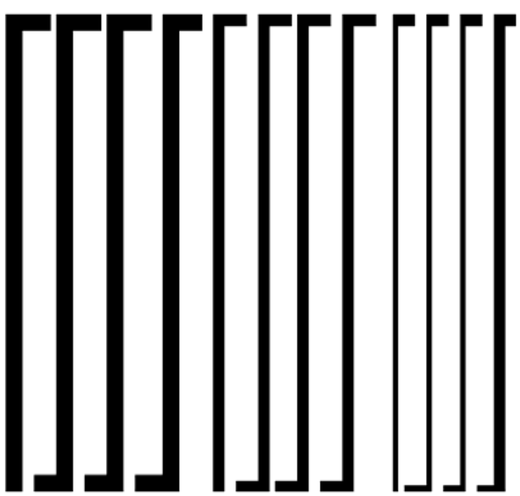


Fig. 1 (b). Mask for Measured Tracks

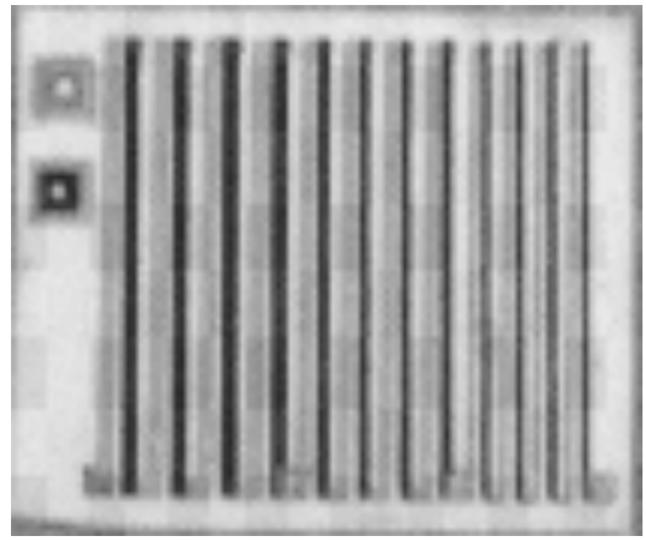


Fig. 1 (c) PdAg/Ag thermopile on Al_2O_3 substrate

3. Measurement circuit and results

The "hot" end of thermocouples junctions was placed on a heater and the "cold" ends on a radiator as is indicated in Fig. 2.

The hot junctions were heated from 293 to 493 K. Correspondingly, the cold junction temperature increased from 293 to 313K. The resultant maximum temperature difference was about 160 to 180K.

We measured E_T = f(ΔT) and R_i = f(T) characteristics. Output electrical power in no-load conditions was evaluated from $P = E_T^2/R_i$ relationship. This paper presents the results for only a few representative structures. To make the comparison easier the thermopiles with reference track made of PdAg and with track wide 0.7 mm were chosen. Additionally thermopiles based on 40vol% RuO_2/60vol.% glass composition with track width 0.5 and 0.3 mm were chosen, to illustrate the influence of track width on the electrical output power. Parameters of selected structures are presented in Table I. All structures consist of four thermocouples. Each was 22 mm in length. PdAg was used as the material for the reference track

The thermoelectric force E_T and output electrical power P for as-made thermopiles as a function of hot-cold junction temperature difference are shown in Figs. 3 (a) and 3(c). Also resistances of structures enumerated in Table 1 versus hot junction temperature are presented in Fig. 3 (b).
The output voltage of RuO_2-based thermopiles is only slight higher than Ag-based ones (several percent). On the other hand, conductor-based thermopiles have internal

resistances one-two orders of magnitude less than resistor-based ones.

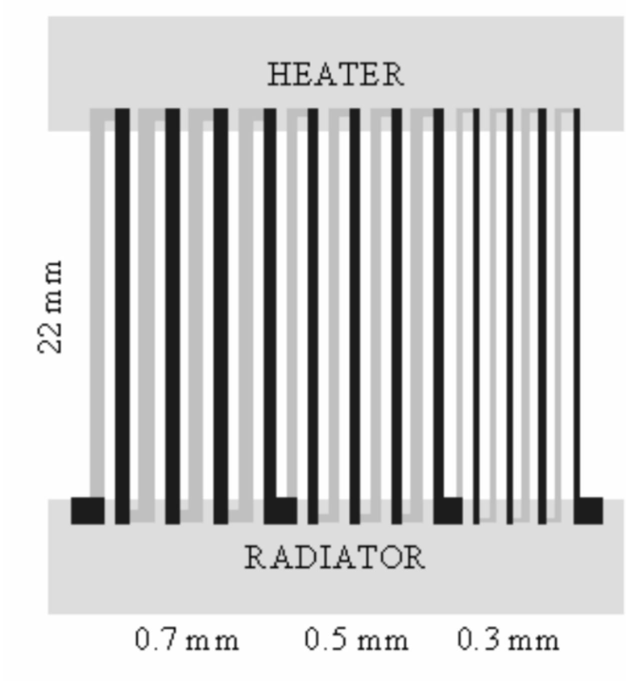
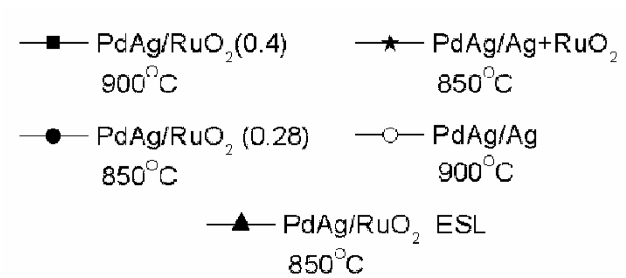


Fig. 2. Measurement Setup

Therefore, PdAg/Ag thermocouples generate greater power than the other composites.



Legend for Figs. 3(a), 3(b) and 3(c).

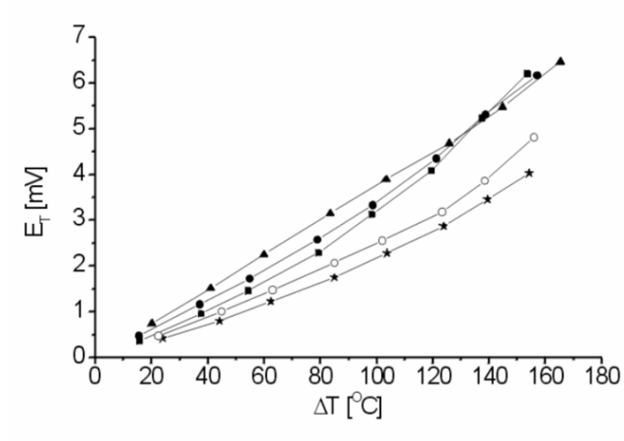


Fig. 3(a). Thermoelectric force E_T as a function of temperature difference

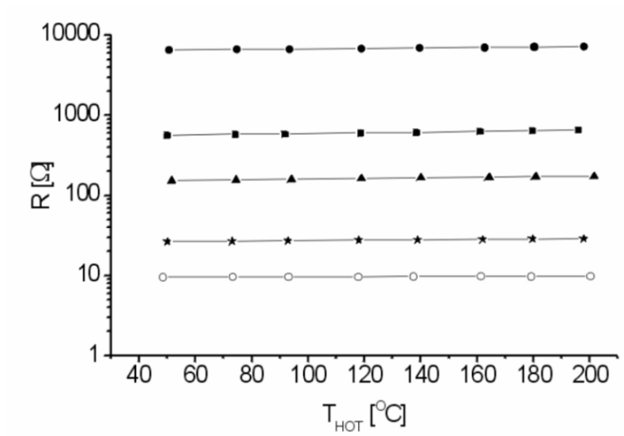


Fig. 3(b). Resistance as a function of hot junction temperature

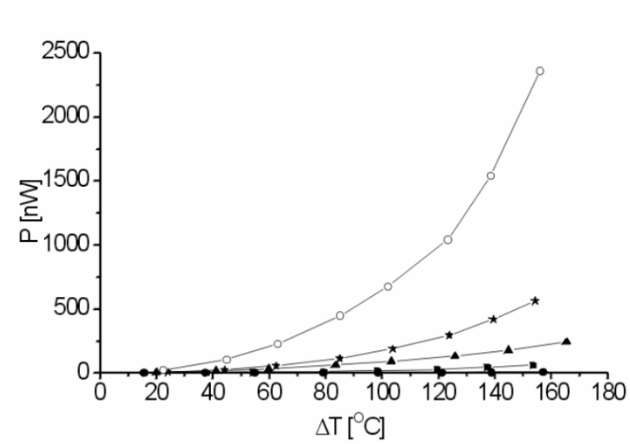


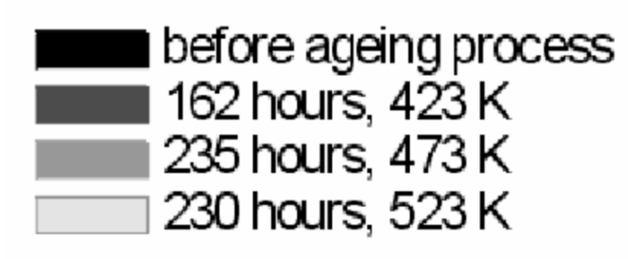
Fig. 3(c) Output electrical power *P* as a function of temperature difference.

Table 1. Characteristics of Tested Composites

Name	Tested track material (second arm)	Firing temperature [K]	Thermocouple width [mm]
A	40% RuO_2	1173	0.7
B	40% RuO_2	1173	0.5
C	40% RuO_2	1173	0.3
D	28% RuO_2	1123	0.7
E	RuO_2 (ESL)	1123	0.7
F	Ag+RuO_2 (DuPont)	1123	0.7
G	Ag	1173	0.7

The change in value of electrical parameters of thermopiles after exposure to long-term ageing processes was also investigated. Three cycles were applied: 162 hours at 423 K, 232 hours at 473 K and 230 hours at 523 K. Pre and post measurements of the electrical characteristics were made. Also results achieved for three different PdAg/RuO_2 (40 vol.% RuO_2) thermopiles are presented (with 0.7, 0.5 and 0.3 mm thermocouple width) to show the influence of track (arm) width on the output electrical power *P*.

Seebeck coefficient, calculated for each type of thermocouples is shown in Figure 4 (a). Before ageing process it was in the range 9 to 11 μV/K for RuO_2-based thermocouples and 6.5 to 7.5 μV/K for Ag-based ones. After the first ageing cycle, the Seebeck coefficient in resistive ink- based structures decreased by about 20 percent. Subsequent cycles had little influence on this parameter. PdAg/Ag+RuO_2 thermocouples experienced a permanent decrease of α, and decreased after each subsequent cycles. The most promising results were exhibited by the Ag-based structures. It seems that ageing has little influence on those thermocouples, and fluctuations of Seebeck coefficient arise from measurement inaccuracy rather then from any real changes.



Legend for Figs. 4(a), 4(b) and 4(c)

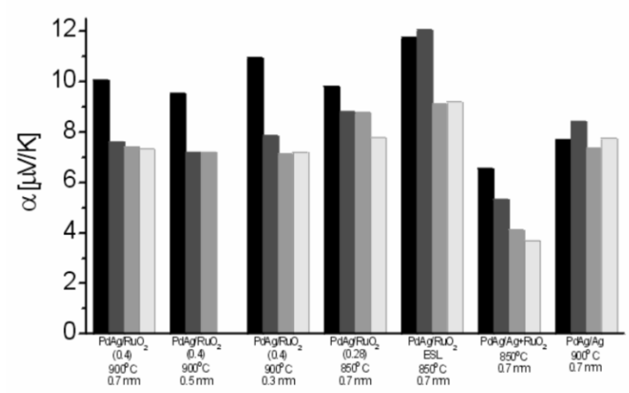


Fig. 4(a). Influence of Ageing Process on Seebeck Coefficient (L->R: A->G)

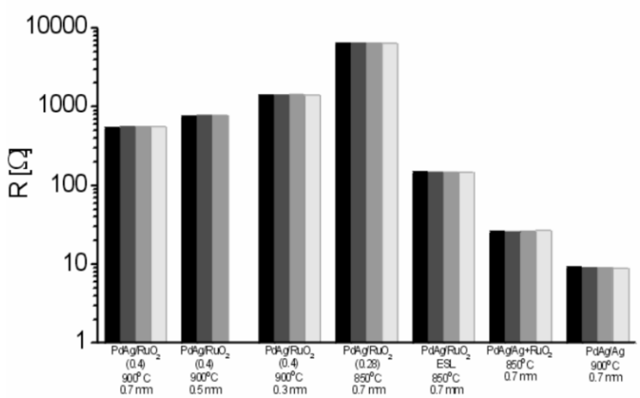


Fig. 4(b). Influence of Ageing on Resistance *R* at Room Temperature (L->R: A->G)

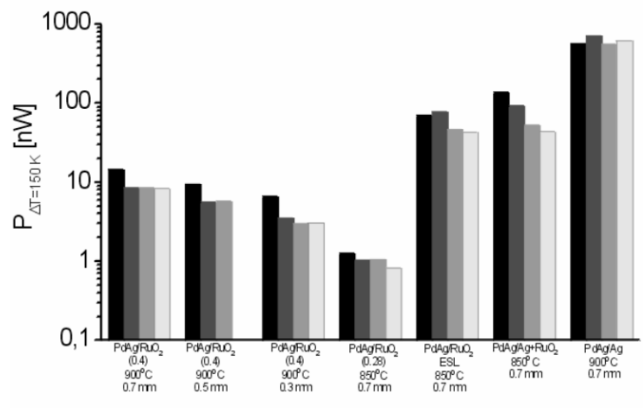


Fig. 4(c) Influence of ageing process on Output electrical power *P* (for temperature difference *ΔT* = 150 K between hot and cold junction) (L->R: A->G)

The influence of ageing process on thermocouples resistivity is negligible as shown in Fig. 4 (b), so changes in electrical output power are influenced only by changes in the Seebeck coefficient. That the reason why Figs. 4 (a) and 4 (c) have very similar plots.

4. Thermoelectric microgenerators based on thick film thermopiles – qualitative analysis

The selection of thermocouple materials for thermoelectric microgenerators is based on maximizing the thermoelectric figure of merit *Z:*

$$Z = \frac{\alpha^2 \sigma}{\lambda}$$

where α - Seebeck coefficient, σ - electrical conductivity, $\alpha^2\sigma$ - power factor, λ - thermal conductivity, or dimensionless figure of merit *ZT*, where *T* is the absolute temperature [5]. Moreover, to be used in a micro system, a thermoelectric generator must be small in size, light in weight and have fabrication technology compatible with other micro system elements.

The figure of merit Z_{AB} of a thermocouple composed of thermocouple materials A and B is defined as [6]

$$Z_{AB} = \frac{\alpha_{AB}^2}{\left(\sqrt{\rho_A \lambda_A} + \sqrt{\rho_B \lambda_B}\right)^2}$$

where α_{AB} = (α_A - α_B) denotes the relative Seebeck coefficient, ρ_A, ρ_B – electrical resistivity of the thermocouples materials A and B, λ_A, λ_B - thermal conductivity of materials A and B.

The above formulas prove that values of all parameters used for *Z* calculation, that is, Seebeck coefficients as well as electrical and thermal conductivities of both thermocouple materials are important in the case of thermoelectric generators. Moreover thermal conductivity of substrate and matching-load conditions should be taken into consideration. Therefore it is not surprising, that currently thick film thermocouples with moderate relative Seebeck coefficients gives larger generated power than mixed (thick/thin) thermopiles with much larger relative Seebeck coefficients [3].

5. Conclusions

The most promising results were achieved for PdAg/Ag thermocouples. Output electrical power of this structure is more then two orders of magnitude higher than the others. It also has good stability after long-term ageing exposure which is a very important factor.

Investigations will continue in increasing our knowledge about thermoelectric properties of thick film materials. To improve properties of thick film thermocouples, an optimization process is required. It should be focused on decreasing the electrical resistance of tracks and contacts which can be achieved by modification of track shapes and dimensions. Also thermal conductance which has an inverse influence on the figure of merit should be lowered.

References

[1] Z. Zhou, C. Uher, "Apparatus for Seebeck coefficient and electrical resistivity measurements of bulk thermoelectric materials at high temperature", Rev. Sci. Instrum., vol. 76 (2005), 023901, pp. 1–5.

[2] S. Duby, B.J. Ramsey, D.J. Harrison, "Printed thick-film thermocouple sensors", Electronics Letters, vol. 41 (2005), pp.312-314

[3] P. Markowski, A. Dziedzic, E. Prociow, "Thick/thin film thermocouples as power sources for autonomous microsystems – preliminary results", Microelectron. Int., vol. 22, no. 2 (May 2005), pp. 3–7.

[4] T.M. Berlicki, "Heat dissipation in thin-film vacuum sensor", J. Vac. Sci. Technol. A, vol. 19 (2001), pp. 325-328

[5] D.M. Rove, "CRC Handbook of Thermoelectrics", London, CRC Press 1996

[6] E. Castano, E.Revuelto, M.C. Martin, A. Garcia-Alonso, F.J. Garcia, "Metallic thin-film thermocouple for thermoelectric microgenerators", Sensors and Actuators A, vol. A60 (1997), pp. 65-67