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History of Development of Thermoelectric Materials for Electric Power Generation and Criteria of their Quality

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An analysis of results, obtained in the development of thermoelectric materials for electricity generation during the last 130 years, shows that they are comparable to those obtained as early as the nineteenth century. One of the main factors responsible for the stagnation in this area is the use of inappropriate criteria for the evaluation of material quality. The most popular criterion used for this purpose is the Thermoelectric Figure of Merit. The criterion of usefulness proposed in this paper is free of imperfections of the Thermoelectric Figure of Merit and may be considered as alternative to it. The criterion of usefulness shows, among other things, that it is reasonable to develop thermoelectric pairs both with high and relatively low thermoelectric efficiency. Its application would make it possible to avoid the creation of useless materials. This is especially important under conditions of limited research funding.

Keywords: *thermoelectric power generation, thermoelectric figure of merit, thermoelectric material efficiency, thermoelectric material performance, thermoelectric material quality*

1. Introduction

The growing concern with the exhaustion of energy resources indispensable to modern life, such as oil, natural gas and coal, feeds the development of new technologies based on the use of alternative natural resources: solar energy, hydroelectric energy, wind energy, bioenergy, geothermal energy, etc.

As to the thermal energy, it occupies a special place in human activities, since it accompanies the majority of industrial processes and processes occurring in the Nature. In most cases, the waste heat is lost without any economic profit. This energy resource does not cost anything and can be used to reduce both the impact of the energy crisis and heating of the environment. Therefore, the conversion of waste heat into electricity is welcome.

The converter of heat into electricity is called thermoelectric generator (TEG) or thermoelectric pile (in the 19th century). The operating principle of the TEG is based on the Seebeck effect discovered in 1821. The scheme of direct conversion of Thermal Energy into Electricity is shown in Figure 1.

The modern TEG represents a pile consisting of a great number of different material A and B pairs connected in series through electricity conductors. The difference in temperatures between two sides of the TEG makes each pair generate an electric potential, and the sum of these potentials is called electromotive force of the pile. Increase in the number of these pairs allows increasing the electromotive force up to the desirable value. The electromotive force of the pile will be greater if the electric conductivity of materials A and B is of a different nature, of the "n" (negative) and "p" (positive) types.

The electricity generators based on the Seebeck effect do not depend on the nature of consumable heat and, therefore, they can be used in different areas.

It is important to note that the device shown in Figure 1 can be used not only for conversion of the heat into electricity, but also for the inverse process. When a current is supplied to this device, it produces the difference in temperatures between its two sides (Peltier effect, discovered in 1834). In this case, the device is called Thermo-Electric Cooler (TEC).

The TECs were developed in the form of Peltier pastilles for small capacity applications and limited space. They are used extensively for controlling the temperature of electronic components and cooling them.

2. Thermoelectric Materials (TMs)

Since Seebeck's discovery, many materials have been considered useful to generate thermoelectricity.

The first TEGs were based on electricity conductors and semiconductors, such as antimony, bismuth, copper, iron, lead, zinc and different alloys, among others[1]. Later, in the 20th century, many other thermoelectric materials (TMs)

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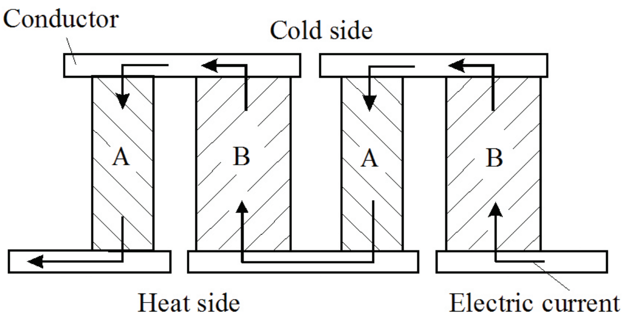

Figure 1. TEG (thermoelectric pile).

were developed: ceramics, composites, etc. Nevertheless, the updated semiconductors continue being basic TMs for the production of thermoelectric effects.

It should be emphasized that all these materials were obtained empirically, through thousands of attempts based on the personal experience of a researcher. Therefore, the essential progress in the TMs area depends mainly on the advances in fundamental knowledge related to the nature of thermoelectric effects.

2.1. Performance of the thermoelectric material

Since the 19th century, engineers had been seeking to build an efficient and economically viable TEG. They perceived that the generator efficiency depended on both of the generator construction and properties of TMs. But it was only in 1909 that Engineer Edmund Altenkirch mathematically expressed the relationship between physical properties of TMs and the efficiency of a simplified thermopile or TEG.

Altenkirch's equation[2] includes, among other parameters and variables, the electromotive force, thermal and electrical resistance/conductivity of a thermopile. Later, in 1949-1956, the famous Russian scientist, Abram F.Ioffe integrated these parameters into the Z group (quantity Z or parameter Z) and used the new parameter Z to calculate the efficiency of thermoelectric devices. The Ioffe's parameter Z is given by the formula[3]

$$Z = \alpha^2 \cdot \frac{\sigma}{\lambda} \qquad (1)$$

where:

Z – complex characteristic of the TM pair properties, [1/K];

α – electromotive force of the thermoelectric device;

σ – electric conductivity of the TM pair;

λ – thermal conductivity of the TM pair.

According to Ioffe, Z is the most important characteristic of thermoelements[4]. This parameter was introduced to calculate the efficiency of devices having the following features[3]:

- device arms are formed by a pair of materials A and B of the p/n type;
- electromotive force of each of materials A and B is the same;
- thermal and electric contact of materials A and B is ideal;
- difference in temperatures between the hot junction and the cold junction of the device is very small;
- physico-chemical properties of materials A and B do not vary with time.

It is very important to emphasize that the Ioffe's "ideal thermoelectric device" is equivalent to a pair of materials A and B being in perfect contact with each other. Therefore, the parameter Z can be also used for the evaluation of the performance of TM pairs. The greater the value of Z, the better a TM pair is.

In practice, the performance of TMs is determined for pairs formed by the material A and the superconductor B (Pb; 0÷7.2K). In this case, the performance of a pair A and B is considered as the performance z only of the material "A". The performance z is expressed by the formula[5]

$$z = \alpha^2 \cdot \frac{\sigma}{\lambda} \qquad (2)$$

It should be emphazised that, unliike the Formula 1, all parameters in the Formula 2 refer to a single material A. The greater the value of z, the better the material is.

In the last six decades, the parameter z is used widely in TM researches. The parameter z is considered as the most important characteristic of TM and is called "Thermoelectric Figure of Merit"[6-8] or TFM. It is accepted that this parameter expresses well the capacity of TMs both for the generation of cold and the direct conversion of heat into electricity. The parameter z serves to facilitate the evaluation of the TM performance and makes the comparison of TMs easier. The TM performance is often expressed in scientific papers as the product of z by temperature T. This product zT is a dimensionless quantity of the TM performance. It should be emphasized that the properties α, σ and λ of material depend on the temperature T of material. Consequently, the TFM is not a number, but a function of the temperature.

Generally, the value of T in the product zT corresponds to the maximum temperature of the TM operation. Thus, the product zT is the maximum value of the performance of material. This value varies from one material to another. According to recent data[9], zT of developed TMs does not exceed 2.4. The typical TFMs of some TMs are shown in Figure 2.

It is noteworthy that these TMs are not used for electric power generation, despite the high value of TFMs. The results of numerous experimental investigations show that the performance of TMs depends not only on its chemical composition but also on the microstructure which is determined in its turn by material processing, especially by

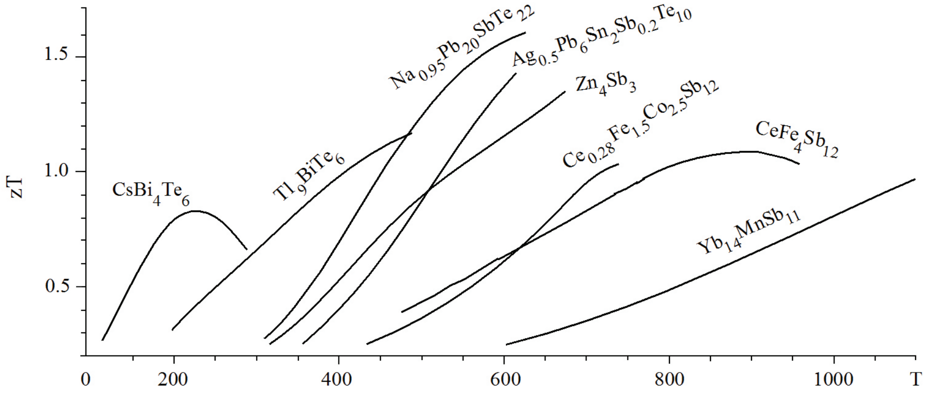

Figure 2. The p-type TMs of academic importance[10-15].

sintering. Basing on these results, many researchers focus their efforts on the development of TMs with sophisticated microstructures. At present, such strategy is used in the following investigations[16]:

a) improvement of traditional TMs already known more than hundred years such as Zinc, Antimonite and Bismuth Telluride;
b) improvement of new classes of TMs (Lead Telluride and Related Compounds; Silicon-Germanium Alloys; Half-Heusler Compounds; Metal Silicides e Boron Carbide; Oxides and others), already having one or several useful physical-chemical properties.

2.2. "Efficiency" of a single thermoelectric material

According to Aldo Vieira da Rosa, the "efficiency"[5] η of a single TM is defined by the equation:

$$\eta = \frac{(1+zT_m)^{0.5}-1}{(1+zT_m)^{0.5}+\frac{T_C}{T_H}} \cdot \frac{T_H - T_C}{T_H} \tag{3}$$

where:

T_H – temperature of the TM pair hot side;

T_C – temperature of the TM pair cold side;

$$T_m = \frac{T_H + T_C}{2}.$$

The η of modern TMs is in the range from 5 to 15%. The laws of physics do not forbid the existence of materials with a greater value of η. Therefore, the development of new materials goes on. The recent technological advances show that modern TMs may significantly surpass photovoltaic cells in the "efficiency" of energy generation[17]. Taking in account the advances in the development of the thermoelectric materials, the "efficiency" of TMs of the new generation may reach 21% within the next few years[18,19].

2.3. Efficiency of the Heat Engine based on a thermoelectric material pair

According to Ioffe, the efficiency h_g of the "ideal thermoelectric device" for electric power generation is defined by the equation[3]

$$\eta_g = \frac{(1+ZT_m)^{0.5}-1}{(1+ZT_m)^{0.5}+\frac{T_C}{T_H}} \cdot \frac{T_H - T_C}{T_H} \tag{4}$$

The efficiency of a real thermoelectric device depends not only on the temperature and the quantity Z, but also on other physical-chemical properties of TMs as well as on the electrical load applied to the TEG and TEG geometry[5]. Therefore, the efficiency of a real thermoelectric device is calculated using the other formula. The efficiency of modern heat engines for electric power generation, based on the TMs is in the range of 2 to 8% (different reference sources). The typical efficiency[20] is around 5%.

2.4. Comparison of the TM pairs efficiency with the efficiency of other heat engines

A great amount of data concerning the "efficiency" of a single TM makes it difficult to evaluate the state of the art in the development of TMs intended for electric power generation.

In order to cope with this problem, the comparison of the efficiency of the "ideal thermoelectric device" formed by a TM pair of the p/n type with the efficiency of turbines has been carried out. The bismuth telluride and the "binary cycle turbine" have been selected for this purpose. The bismuth telluride is mainly used for cooling, but they can be also used for electric power generation at the low temperature range (300-450K). As to the binary cycle turbines, they are intended for capturing the low grade heat and are used in geothermal power plants (300-450K).

The results of the comparison are shown in Figure 3 plotted for the temperatures T_C=300K and T_H=450K.

The solid curve shows the "efficiency" η calculated by the Equation 3 for any TM with zT_m from 0.9 to 1600. The horizontal dashed line corresponds to the maximum theoretical "efficiency" η =33.3% ($zT_m \rightarrow \infty$). The point s of this curve corresponds to the "efficiency" of bismuth telluride (zT_m=0.9). The grey horizontal band shows the efficiency of the binary cycle turbine[21] (η =12-16%).

As one can see from Figure 3, the efficiency of any TM pair with zT_m from 0.9 (bismuth telluride) to 3.9 (some hypothetical TM pair) operating at the low temperature range is less than the efficiency of the "binary cycle turbine".

The calculations show that the efficiency of TMs pairs operating at the intermediate and high temperature range is many times less than that of the the modern steam turbine.

3. TMs and TEGs for Industrial Use

Since the discovery of thermoelectric effects, numerous TEGs (piles) have been created in several countries, but only some of them were implemented in the industry. The first successful attempt was made by M.G. Farmer, who exhibited two of his models at the Universal Exhibition of 1867 in Paris.

These piles were based on a pair of the TMs called “German silver” (Cu60%, Ni20% and Zn20% - negative material) and antimony-zinc alloy (positive material). The Farmer’s piles were used in the industry for several years. But the rapid loss of their capacity and the thermoelectric bar fragility prevented their widespread use[22,23].

Other piles most known at that time were developed by engineers Charles Clamond and Louis Mure.

The second version of Clamond and Mure pile was based on the alloy of Marcus (Zn66.6% and Sb33.3% - negative material) and on iron (positive material). It surpassed all other similar piles and won the Gold Award of French National Industry[24,25]. In 1876, the “Thermo-Electric Generator Company” (France) began the mass production of Clamond’s generators (piles). But soon it turned out that generators had serious problems: the TM melted and oxidized rapidly as well as exfoliated at the cooling of the hot junction[26,27]. These deficiencies of TMs affected the generator efficiency.

Clamond needed four years to develop new TMs and alterate the construction of vulnerable elements.

His new TEG called “Clamond Improved Thermopile” was based on the alloy of bismuth and antimony (negative material) and on iron (positive material). This efficient and powerful generator was free of all imperfections of its prototypes and was the best TEG at that time[23,24,28,29].

On May 1879, the new Clamond’s generator was presented to the French Academy of Sciences.

Several monthes after, Clamond transferred the complete control over this generator to the well-known industrial group engaged in the field of electric light and telecommunications. As a result of this transaction, his research activity in the field of thermoelectricity was stopped, and the best TEG of the 19th century was never used in the industry.

The early TEGs were widely used for obtaining the electric light, electro-depositing, electro-plating, electrorefining, charging secondary batteries and for telegraphic and printing purposes. As to the cost of the electricity generated by these devices, it was from two to four times higher in comparison with dynamoelectric machines[29]. Therefore, the TEGs lost to the competition, and the development of TMs for TEGs was interrupted for decades.

The research in the field of thermoelectricity was revitalized in connection with the need for the development of military technologies, space flights and cooling technologies. Since 1954, many new TMs have been developed. Despite these advances, there are very few industrially useful TMs. The commercialized TMs are shown in Figure 4.

The Figure 4 clearly shows that the amount of commercialized materials is negligible. This gives evidence for a long period of the stagnation[31] in the TMs development.

Today, the most popular TM is bismuth telluride[16]. This material is mainly used for cooling and for controlling the circuit temperature at relatively low temperatures. The optimal temperature for the use of bismuth telluride is about 450 K. But, as the maximum operating temperature for this material is 550-600K, it can also be used to generate electricity.

The intermediate temperature range (about 900K) is the most appropriate for materials based on alloys of lead. As to the high temperature range, it is occupied by the Silicon-Germanium (SiGe) Alloys. These TMs can operate at temperatures up to 1300K. The two latter materials are used in the radioisotope TEGs.

The modern TEGs are used to supply electricity to satellites, space probes, navigational aids, communication systems and safety equipment for offshore installations as well as to provide the cathodic protection of gas pipelines.

The world market of TEGs in 2012 is presented in the Table 1.

The main characteristics of early and modern TEGs are shown in the Table 2.

As shown in the Table 2, the efficiency of the Clamond’s TEG (pile) was 4.8÷5.0%. This value was confirmed in

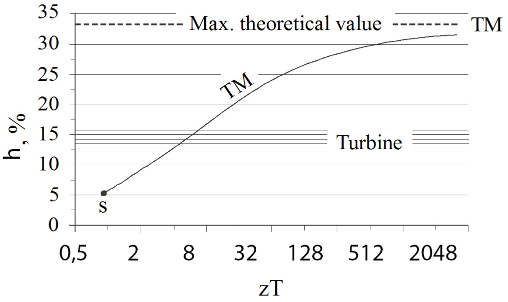

Figure 3. Comparison of the TM “efficiency” with the “binary cycle turbine” efficiency (T_C=300K, T_H=450K, zT_m from 0.9 to 1600).

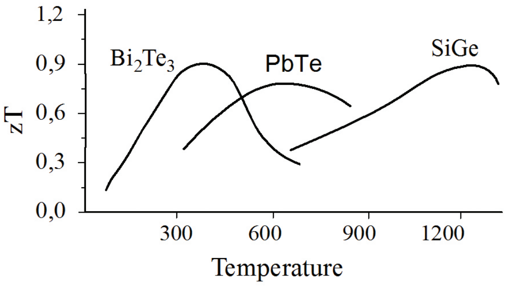

Figure 4. Commercialized TMs[30].

Table 1. World market of TEGs (in 2012)[32].

Segments	Volume, %
Military and Aerospace	96
Other industrial areas	2
Other non-consumer	2
All segments	100

Table 2. Characteristics of TEGs taken from reliable sources.

Year	Inventor / Manufacturer	h_g* (%)	Material	T_{max}	Heater	TEG model
1879	Clamond, C.	4.8÷5.0	SbBi/Fe	723	The coal	Clamond's pile[24,28]
1887	Gülcher, R.J.	4.31	ZnSb/Ni	**	Gas	Gülcher*'sche* Säule[28]
1964	NASA	1.47	SiGe/PbTe	777	U-235	SNAP-10A[33]
1964	Voronin, A.N.	2.0	ZnSb/CuNi	690	Natural gas	ТЭГ-50[34]
1968	NASA	5.0	PbTe/PbTe	866	Pu-238	SNAP-27[35]
2012	Everredtronics	5.0	BiTe/BiTe	570	Any heater	TEG 241-60B[36]
2012	NASA	7.6	TAGS/PbTe	823	Pu-238	MMRTG[37]

*Efficiency values for a generator as such; **T_{max}<903K (melting temperature of antimony); accurate data are not available.

1881, by an electrical engineer Edouard Hospitalier[38] who was a professional in the field of thermogenerators. But according to the modern historiography, the efficiency of 19th century TEGs was (0.5-1.5%)[39-41]. However, both evaluations are correct.

Engineers of 19th century calculated the efficiency of the system "generator & heater"[28,42]. It is easy to comprehend that the results of these calculations are related to two components of the system: generator and heater. For example: efficiency of the Clamond generator is 4.8%; efficiency of the Clamond heater (furnace) is 13.54%; efficiency of the Clamond "generator & heater" system is (13.54 × 0.048) = 0.65%.

As to the modern approach to the efficiency calculations, it is related to a generator as such.

In this case, the result of calculations does not depend on the heater. Therefore, the efficiency values calculated for the same generator by different methodologies are correct on their own, but not equal. It is worth adding that the manufacturing processes of outdated generators were simpler and cheaper than those of modern ones.

According to Ioffe, the techno-economic feasibility of the TEG is defined by four main characteristics: the TEG durability, its cost, TM performance and operating temperature limits. Other characteristics (generator power and electromotive force) are secondary. They depend on the generator construction and can be easily altered[4].

As to the possible low efficiency of the TEG to be developed, this imperfection can be compensated by increasing the generator size and/or by using the waste heat[16] (residual heat, geothermal heat, etc.).

4. Imperfections of the Concept of Thermoelectric Figure of Merit

In the last 190 years, various approaches to the evaluation of the performance of TMs were used (Zeebeck, T., 1822; Rayleigh, L., 1885; Justy, 1948; Meissner, 1955)[3]. Currently, the use of the TFM is the most popular for this purpose. However, the concept of the TFM is only good for the evaluation of hypothetical TMs, the physico-chemical properties of which do not change with time.

But the practice shows that the performance and efficiency of TM pairs operating under high temperatures is reduced over time due to the aging of TMs. The negative changes of TM properties (mechanical, chemical, microstructure and etc.) are caused by the following factors:

a) vibrations as well as thermal shocks and stresses accompanying the operation of a thermoelectric device;
b) aggressive agents present in the environment, such as oxygen and air humidity;
c) alteration of the chemical composition caused by diffusion;
d) alterations of the crystalline structure caused by high operating temperatures.

As one can see from the Formula 2, the TFM desregards all listed factors.Therefore, the use of the TFM for the evaluation of the performance of real TMs intended for the electric power generation may end in failure. The Table 3 shows that the "efficiency" η of the TMs with a large value of *z* may be smaller than that with a small value of z.

Often it turns out that the material with the high Thermoelectric Figure of Merit is useless in practice[5].

Thus, apparently, the TFM is not an adequate criterion for the evaluation of the performance of real TMs. Therefore, the development of more appropriate criteria for evaluating the TMs and real TM pairs continues.

For example, in 2011, a team of Russian researchers proposed a new criterion (Lidorenko-Tipikin-Kolomoyets criterion k)[43] for evaluating the efficiency of TM pairs. This criterion, based on a new combination of TM properties, is given by the formula

$$k = \frac{\alpha}{\frac{\lambda}{\sigma} + \alpha^2 \cdot T_M} \tag{5}$$

where T_M is the average temperature of TM pairs; the parameters α, σ and λ refer to TM pairs inside a real TEG.

The greater the value of k, the better TM pairs /TEG is for the practical use. Though the criterion k is more appropriate for the development of real TEGs than the Ioffe's parameter Z or FTM, nevertheless, it does not include some principal characteristics of TM pairs: their durability and cost.

It should be emphasized that the modern concepts for evaluating the TMs or real TM pairs are based on the preferences of their authors. Therefore, it is quite likely that new concepts may appear in the future.

5. Criterion of Usefulness of TM Pair

It was shown above that the Ioffe's parameter Z, the Thermoelectric Figure of Merit z and the Lidorenko-Tipikin-Kolomoyets criterion k are not quite suitable for the

Table 3. Performance and "efficiency" of some TMs5.

MT	$z{\cdot}10^3$	$(T_H)^*$	T_C	zT_H	η (%)
Bi_2Te_3	2.0	450	300	0.9	5.4
$BiSb_4Te_{7.5}$	3.3	450	300	1.5	7.6
Bi_2Te_2Se	2.3	600	300	1.38	11.1
PbTe	1.2	900	300	1.08	12.6
CeS (+Ba)	0.8	1300	300	1.04	14.3

$^*(T_H)$ - optimal operation temperature of TM.

correct evaluation of TMs intended for the electric power generation. To fill up this gap in the Material Sciences and Engineering, the authors of the present paper developed a new criterion P, called "criterion of usefulness of a TM pair". This criterion takes into account all the parameters of TMs/TEGs, mentioned by Ioffe[4], including the durability and cost. The criterion P is defined as

$$P = \frac{D}{c} \cdot d \cdot \left[\frac{\alpha^2 \cdot \sigma}{\lambda} \right] \tag{6}$$

where:

P - criterion of usefulness of a TM pair, $\left[\frac{s \cdot kg}{K \cdot \$}\right]$;

D - durability of a TM pair, [s];

c - TM pair cost, [$/kg];

d - aging dimensionless coefficient expressing the decrease of the real TM pair efficiency in the run time D; 1> d >0.

Apparently, the parameter c can be easily obtained from diverse sources including the internet. The durability D is given by researcher. The aging coefficient d is calculated as the ratio between efficiencies ($\alpha^2{\cdot}\sigma/\lambda$) of a TM pair determined at end and beginning of experiments. The methods of accelerated testing of MTs and corresponding equipment are well known.

The parameters α, σ and λ refer to a real TM pair (in the start time of the electricity generation process). Thus, the expression in square brackets describes the efficiency of a real TM pair, but not the efficiency of Ioffe's "ideal thermoelectric device". The greater the value of P, the better a TM pair is for the practical use.

On the whole, the proposed criterion P characterizes a real thermoelectric pair in the real process of the electricity generation. It differs essentially from the TMF and shows that the development of a useful TM pair is considerably more difficult problem than the development of a single material, described in the section 2.1.

6. Conclusion

The results obtained in the development of TMs for electric power generation in the last 130 years are comparable to those obtained in the 19th century by the first inventors of TMs/TEGs. The stagnation in the development of TMs/TEGs is due to economic and scientific factors:

- Since the end of the 19th century, the TEGs have not been able to compete with traditional electric generators based on the use of heat as the energy source. For this reason, the development of TMs was not being considered economically viable.
- The extremely low level of investment slowed down the development of TMs.
- The use of the Thermoelectric Figure of Merit during the last decades as a main tool for the evaluation of the TM performance favored the creation of a great amount of useless materials. It is probably for this reason that, currently, there are few TMs of industrial interest.

Nevertheless, current conditions for the development of usefull TMs are much better than those of the 19th century. The significant progress has been achieved in material science and material processing technology. The advanced equipment for research of materials has been developed. In addition, modern research teams consist of highly qualified specialists and studies of TMs are focused in a few promising areas. Therefore, it is very likely that future research in these areas will lead to success.

As to the criterion of usefulness proposed in this paper, it is free of TFM imperfections and may be considered as alternative to the TFM. This criterion takes into account all the parameters determining the techno-economic feasibility of the TM pairs and TEGs. Therefore, it characterizes the suitability of TM pairs for their practical use. The criterion of usefulness shows, among other things, that it is reasonable to develop thermoelectric pairs both with high and relatively low thermoelectric efficiency. In the latter case, thermoelectric pairs have to be composed of cheap and/or high durability materials. The criterion can be also used for the correct comparison of different TM pairs. Its application would make it possible to avoid the creation of useless TMs. This is especially important under conditions of limited research funding.

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