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Some Notes on the Possible Application of Thermoelectric Devices to the Generation of Electric Power

by

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SOME NOTES ON THE POSSIBLE APPLICATION OF THERMOELECTRIC DEVICES TO THE GENERATION OF ELECTRIC POWER

by

P. J. Bateman, B.Sc., A.Inst.P.

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SUMMARY

heat ?

When waste head is available in a convenient form, conversion to useful electrical power should be possible by means of thermoelectric devices which, fabricated from semiconductor materials already developed, should give a power output per unit weight comparable with that of conventional small d.c. power sources. This can only be realised in practice if installation and construction problems can be overcome, and the effective hot and cold junctions are of the order of 1 cm apart. Efficiencies are, however, so low at present that it is unlikely that thermoelectric devices will be produced for the large scale production of electrical power.

APPENDIX

LIST OF ILLUSTRATIONS

1 INTRODUCTION

If two dissimilar materials are connected to each other at two points to form an electric circuit, and the two junctions are maintained at different temperatures then, depending on the thermoelectric properties of the two materials, a current will flow in the electric circuit. If a resistive load is now included in the circuit, electrical energy will be dissipated in the load. A thermoelectric generator of this type may have application in systems where waste heat may be utilised by direct conversion into electrical energy and used to supply or control devices within the system. Since the thermoelectric effects are reversible they might also be applied to local refrigeration or temperature control systems.

It is the purpose of this note to examine the possibilities offered by thermoelectric devices and to discuss the present position and future prospects in the field.

2 THE NATURE OF THE THERMOELECTRIC EFFECT

When a circuit is formed by two dissimilar materials and the junctions are maintained at different temperatures by some external agency, two types of thermoelectric effect may be apparent:-

(1) The Seebeck effect

This gives rise to an electromotive force in the circuit by virtue of the temperature difference between the two junctions. The reverse effect, known as the Peltier effect, causes heat to be emitted at one junction and absorbed at the other when an electric current is passed through the circuit.

(2) The Thomson effect

This gives rise to an e.m.f. in any element of material which supports a temperature gradient. This effect is usually small compared with the Seebeck effect over the range of temperature differences for which thermo-couples may most usefully be employed.

The ratio of change of the total e.m.f. in the circuit with change in temperature difference between the junctions is known as the Thermoelectric Power α of the circuit.

The Efficiency η of a thermoelectric generator is the percentage of the rate of consumption of thermal energy which is delivered to the load as electrical power. Thus for a generator of high efficiency, materials are required which have a high value of thermoelectric power α and which have low values of thermal conductivity k, so that for a fixed temperature difference between the hot and cold junctions a minimum of heat will be lost irreversibly by conduction down the branches. For a given load the maximum efficiency is achieved with a generator having minimum internal impedance; this demands thermoelectric materials of low specific resistivity ρ.

It can be shown that the parameter $Z = \frac{\alpha^2}{k\rho}$ is a convenient figure of merit with which to describe thermoelectric materials* (Refs.1 and 2.)

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* Some British workers use the square root of this value, viz. $\frac{\alpha}{\sqrt{k\rho}}$.

The most suitable metals with $\alpha \sim 40\ \mu V/^{\circ}C$ have a value of Z around $0.3 \times 10^{-3}/^{\circ}C$ which leads to efficiencies of only 1% for generators using these materials. Thermoelectric generators really only become a practical proposition when efficiencies approaching 10% can be achieved and, with existing semi-conductor materials which have values of Z greater than 1×10^{-3}, this should be possible.

3 THE CHOICE OF THERMOELECTRIC MATERIALS

The properties which affect the figure of merit are all functions of the carrier concentration n, that is, electrons or, in the case of some semi-conductors, "positive holes". The electrical conductivity $\sigma = \frac{1}{\rho}$ is roughly proportional to n whilst the thermoelectric power α tends to zero when n tends to infinity, and α tends to infinity when n goes to zero. But when n is reduced to zero ρ is very large and hence the figure of merit might not be increased. Electron theory indicates that $\frac{\alpha^2}{\rho}$ will be a maximum when $n \sim 10^{19}\ cm^{-3}$, which is 1000 times smaller than for metals and is in the realm of semiconductors. It can be shown also that the optimum value for α is around 200 $\mu V/^{\circ}C$. The thermal conductivity k of a substance is the sum of two parts: that due to the free carriers k_{el} and proportional to n, and that due to lattice vibrations k_{ph} (phonons) which is independent of n. At the concentration $n = 10^{19}\ cm^{-3}$, k_{el} is small. For a large figure of merit Z to be obtained, a high value of the ratio $\frac{\sigma}{k}$ is required coupled with a large value of α. The minimum value of k is given by k_{ph}, which is obtained when n is zero, but we must accept a small n since σ must be as large as possible. Now $\sigma = n u e$, where u is the carrier mobility and e is the carrier charge, so we need carriers of high mobility. High values of u are found in inter-metallic compounds of medium atomic weight, e.g. indium antimonide, and low values of k_{ph} are found in compounds and alloys of the heavy elements particularly in the middle groups of the periodic system.

Since α^2 varies more rapidly with n than do σ and k, it is possible to "dope" the material with carriers (assuming there were too few carriers present initially) to give a favourable value of α. This treatment may also increase the ratio $\frac{\sigma}{k}$, which may be further improved by a reduction of the lattice thermal conductivity k_{ph} by the addition of an impurity compound which crystallises into the lattice in such a way that phonons are scattered, but electrons, with their longer wavelengths, are not affected, and their mobility is unaltered*.

The materials used for thermoelectric generation are intermetallics of Pb, Hg, Bi, Tℓ and possibly Sb, with Re, Se and S. The most advantageous arrangement is for one branch of each thermocouple to be an n-type semi-conductor (having an excess of carrier electrons) and the other to be a p-type semiconductor (having a deficit of carrier electrons, that is, an excess of positive holes). Bismuth Telluride has been gradually developed (Refs.3-7) until an alloy $Bi_2\,Te_3 - Sb_2\,Te_3$ has now been produced which gives an overall figure of merit for a p-n junction of $2.4 \times 10^{-3}/^{\circ}C$. If this could be incorporated into a generator with the junctions operated at 600°K and 300°K the optimum efficiency of the device would be 11.4%.

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* Up till 1954 materials of high thermoelectric power had been selected and an impurity added to decrease the resistivity and also the brittleness (Ref.8).

Given a material of high figure of merit, it might be possible to reduce the thermal conductivity without affecting the electrical conductivity by obtaining the material in powdered or laminated form.

4 THE APPLICATION TO A THERMOELECTRIC GENERATOR

The efficiency of a thermoelectric generator η is given by $\eta = \frac{W}{Q_a}$, where W is the useful electrical power delivered to the load, and Q_a is the net amount of heat absorbed by the hot junction per unit time.

Considering a single thermocouple connected to a load R, we have that, following Joffe (Ref.1):-

$$\eta = \frac{W}{Q_a} = \frac{W}{Q_1 + Q_h - \frac{1}{2} I^2 r} \qquad (1)$$

where Q_1 is the rate at which Peltier heat is absorbed at the hot junction at temperature T_1 due to the current I passing through the circuit. This is equal to $\alpha I T_1$. Q_h is the rate at which heat is conducted down the branches from the hot junction to the cold junction at temperature T_o.

Thus

$$Q_h = (k_1 S_1 + k_2 S_2)\left(\frac{T_1 - T_o}{L}\right) = K (T_1 - T_o) \qquad (2)$$

where k_1, k_2 and S_1, S_2 are the thermal conductivities and cross-sectional areas of the two branches respectively, and L is their length. K is therefore a lumped constant. The term $\frac{1}{2} I^2 r$ in equation (1) represents half the Joule heat which is dissipated within the thermocouple of impedance r and which, as an approximation, may be taken to appear at the hot junction.

Now

$$I = \frac{\alpha(T_1 - T_o)}{R + r}$$

where R is the load impedance and putting $m = \frac{R}{r}$, we obtain

$$Q_1 = \frac{\alpha^2 T_1 (T_1 - T_o)}{r(m+1)}$$

and

$$W = \frac{\alpha^2 (T_1 - T_o)^2 m}{r(m+1)^2}$$

Substituting these values in equation (1) we get

$$\eta = \frac{T_1 - T_o}{T_1} \cdot \frac{\frac{m}{m+1}}{1 + \frac{Kr}{\alpha^2} \cdot \frac{m+1}{T_1} - \frac{T_1 - T_o}{2T_1 (m+1)}} \cdot \tag{3}$$

For an arbitrary value of m the maximum efficiency is given when Kr is a minimum and this occurs when

$$\frac{\rho_1 k_2}{\rho_2 k_1} = \left(\frac{S_1}{S_2}\right)^2$$

whence

$$Kr = \left(\sqrt{k_1 \rho_1} + \sqrt{k_2 \rho_2}\right)^2 \quad \text{and} \quad z = \frac{\alpha^2}{\left(\sqrt{k_1 \rho_1} + \sqrt{k_2 \rho_2}\right)^2} \cdot$$

For a given value of internal resitance r, the maximum delivery of power occurs when $R = r$; but the maximum efficiency occurs for $R > r$, in fact, for a value of m given by $\left(\frac{R}{r}\right)_{opt} = M = \sqrt{1 + \frac{1}{2} z (T_1 + T_o)}$. (4)

In practice M will vary between 1 and 2. The gain in efficiency obtained by optimising the ratio $\frac{R}{r}$ rather than taking $R = r$ may be up to 1% of the total energy dissipated. When $R = r$ the efficiency is given by

$$\eta = \frac{T_1 - T_o}{T_1} \cdot \frac{2T_1 z}{8 + z (3T_1 - T_o)} \cdot \tag{5}$$

Substituting the value of z obtained from equation (4) into equation (3) we get

$$\eta_{opt} = \frac{T_1 - T_o}{T_1} \cdot \frac{M - 1}{M + \frac{T_o}{T_1}} \tag{6}$$

The first factor in equation (6) corresponds to the thermodynamic efficiency of a reversible engine, and the second represents the reduction of this efficiency due to losses by thermal conduction and Joule heat. It should be noted that both factors are increased by raising the temperature T_1.

In order to achieve the maximum possible efficiency then, only one condition has to be satisfied, namely, that the materials chosen should have the highest possible value of z compatible with the temperature T_1 of the heat source; that is, $z \frac{(T_1 + T_o)}{2}$ should be a maximum. Fig.1 taken from Ref.1 shows a plot of optimum efficiency η against T_1 for various values of z assuming $T_o = 300^\circ K$.

Referring to equation (1), it is usually found for small currents that Q_h is the dominant term in the denominator, thus

$$\eta \simeq \frac{W}{Q_h} = \frac{WL}{N(k_1 S_1 + k_2 S_2)(T_1 - T_o)}$$

where N is the number of thermocouples comprising the generator. It should be noted that the electrical power W which is dissipated in the load is also proportional to N, so that the efficiency of the generator is independent of the number of thermocouples of which it is composed. Suppose $k_2 = k_1 = k$ and $\rho_1 = \rho_2$, then $S_1 = S_2 = S$ and we have the power output from each thermocouple equal to

$$\frac{W}{N} = \frac{2 k S \eta (T_1 - T_o)}{L}.$$

Thus the electrical power generated by each thermocouple depends not upon S and L separately, but only upon their ratio. For a given power required this means that the length of the thermoelements is determined by the area available for heating the hot junctions. Also, the power obtainable per unit volume increases as L^{-2}, and is limited only by the restrictions that the electrical resistance of the junctions must be small compared with the resistance of the arms of the thermoelements, and that the temperature drops between the heat source and the hot junctions of the thermoelements and the heat sink and cold junctions must be small compared with the temperature drop between hot and cold junctions of the thermoelements. There may also be mechanical limitations on the length L imposed by the brittleness of the semiconductor material, and the allowable distortion of the generator due to thermal expansion, since the shorter the arms of the thermoelements, for a given temperature difference between hot and cold junctions, the greater the curvature of the slab of elements forming the generator.

5 THE CHARACTERISTICS OF SOME EXISTING THERMOELECTRIC DEVICES

The constructional details of thermoelectric generators are only available for some of the early devices which were very inefficient in regard to power output per unit volume. A Russian generator designed to operate a radio receiver from a standard oil lamp gave an output of 1.62 watts at the rate of only 0.01 watt/cc of thermoelectric material, but this was by no means an optimised design. 3000 thermocouples were used in the device, the cross-sectional area of those in the heater circuit being 6.4 × 5.1 mm to carry 0.5 amp at 1.2 volts and those in the anode circuit being 1.6 × 1.6 mm to supply 0.011 amp at 90 volts. The thermoelements were of constantan in the form of braided wire, and zinc antimonide, in proportions 35 Zn : 65 Sb with 3% of Pb to decrease resistivity and increase the strength. The thermoelement blocks were sintered into the form shown in Fig.2 with the separate elements insulated with asbestos lagging. The thermocouple arms were 2.20 cm long and during operation the temperature difference maintained across them was 200°C. Another type of generator of similar size and construction was capable of giving an output of 5 watts. In addition, a generator giving 15-20 watts, again from a kerosene burner, has been produced to feed radio transmitters. The Russians are also manufacturing generators of 200 and 500 watt capacity, and a 100 watt experimental solar thermoelectric generator is already in operation (Ref.1).

An early American device built as a solar thermoelectric generator gave an output of 0.165 watts for a temperature difference of 46°C (Ref.9). The thermoelements were 2.5 cm in length and comprised bars of zinc antimonide and an alloy of 91 bismuth 9 antimony. Here the power output per unit volume was only 0.0017 watt/cc, the limiting factor on the size of the thermoelements being the mechanical strength of the alloys.

Recently the Americans have disclosed details (Ref.10) of a 5 watt thermoelectric generator weighing 2.3 kg which was suitable for powering radio transmitters in satellites and rockets. The heat was produced by the absorption of Polonium alpha particles which established a maximum temperature difference of 400°C between the hot and cold junctions, and the efficiency of conversion of heat into electrical energy was 5%. The device had a smaller surface area than an equivalent solar (photovoltaic) battery.

Recent work on commercial thermoelectric devices has been to produce domestic refrigerators employing the Peltier effect. A Russian water cooled unit (Ref.1) contained around 50 gm of semiconductor material and consumed approximately 50 watts. Other applications included a thermostatic device for electronic equipment featuring automatic cooling and heating.

In the United Kingdom the only reported work on recent practical devices has been that of an experimental unit for the cooling of individual components of an electrical circuit. Efficiency of operation of the circuit might be lost if all the components had to be maintained at the maximum operating temperature of the most temperature-sensitive component. Bismuth telluride n and p type elements having a figure of merit of $1.1 \times 10^{-3}/°C$ were used. Each element was of dimensions 3 x 5 x 7 mm, and difficulties associated with the extreme brittleness of the material and the adhesion of the copper strips linking the junctions were overcome in this particular design application.

6 THE MERITS AND APPLICATION OF THERMOELECTRIC DEVICES

The advantages of thermoelectric devices are that they can be used to convert into useful electrical power heat energy which would otherwise be wasted, they contain no moving parts, they are silent, they should require no servicing during use, and a long operational life may be expected from them. Their low efficiency renders them unsuitable for the large scale generation of electric power, but for certain applications they become a practical proposition when one or other of their advantages is a design requirement.

A design study is given in Appendix 1 for a 100 watt thermoelectric generator giving an output of 4 amps at 25 volts. The form of construction was taken to be similar to that illustrated in Fig.3. The weight of such a generator is shown in Fig.5 as a function of temperature difference between hot and cold junctions, the figure of merit for the thermoelement materials, and the length of the thermoelement arms. By comparison, an existing nickel-cadmium cell, one of the most compact types for high discharge rates, having a weight of 700 gm and a volume of 200 cc, is capable of delivering 120 watts at 20 volts for only 2½ to 3 minutes. A 24 volt 4 ampere-hour lead acid accumulator would weigh 2.8 kgm.

From Figs.4 and 5 it can be seen that a 100 watt thermoelectric generator made from materials of a figure of merit of 2.5×10^{-3} and with arms 0.4 cm long supporting a temperature difference of 200°C, would weigh about 600 gm and would have a surface area of hot junctions of 150 sq cm. Assuming a coefficient of expansion of $2 \times 10^{-5}/°C$ for the semiconductor materials the generator, if in the form of, say, twelve strips 1 cm wide, would bow to a radius of 100 cm. If each strip were freely supported at say its centre this would involve the edges of each strip moving about 2.0 mm from the quiescent plane. If this movement were restricted by clamping, the thermal stresses set up might be sufficient to cause cracking of the thermoelements. It is possible that this might be overcome to some extent by the use of a plastic material for insulation of the elements.

It does appear then that, provided temperature differentials of the order of 200°C or greater are available, there is a strong possibility that thermoelectric generators, after a comparatively short period of research and development, could compete on a weight-for-weight basis with more conventional sources. The problems to be considered in the installation of the generators will be the construction and mounting difficulties, the absolute temperature level at which the temperature differential is obtained and the fact that this differential may only exist for a short time.

It should, however, be emphasised that such devices would be harnessing a source of heat which is available as a result of the degradation of mechanical, electrical or chemical energy in some primary process such as propulsion or room heating, and where a convenient heat sink is also available. It is only in these circumstances that the favourable weight-for-weight comparison is justified, since no account has been taken of the weight of the heat source or the means by which the heat is supplied to and rejected from the thermopile, for example, ducting or cooling fins. In certain specialised applications as in the American nuclear fuelled generator (Ref.10) where the long life makes a thermoelectric device attractive as a primary source of power, the weight comparison discussed above is no longer valid since here the weight of the heat source is an appreciable fraction of the weight of the complete unit.

It should not be forgotten that thermoelectric devices can also be used for refrigerating small components quite economically (the same criteria hold for their design as for generators) and also for controlling the temperature of, for example, electronic equipment, by regulating the direction of current flow through the thermoelectric elements.

7 CONCLUSIONS

Once engineering and production difficulties have been solved it is possible, using materials which have now been developed, that thermoelectric devices can be produced which can give a small but useful supply of electricity at the expense of no great bulk provided that the heat source and sink are available in a convenient form. A satisfactory power to weight ratio compared with conventional power supplies can be achieved if the hot and cold junctions are of the order of 1 cm apart, and the successful operation of the devices will depend on their being satisfactorily mounted thermally, electrically and mechanically. Efficiencies are not greater than about 10 per cent at present, and this will prohibit their use for large scale production of electricity, but even with efficiencies as low as 5 per cent thermoelectric devices have been used as small primary sources of electric power in applications where their long life without attention has proved attractive.

LIST OF SYMBOLS

α thermoelectric power $\frac{\Delta E}{\Delta T}$

η thermoelectric efficiency $\frac{W}{Q}$

k thermal conductivity

σ electrical conductivity

LIST OF SYMBOLS (Contd.)

ρ	specific resistivity $\frac{1}{\sigma}$
r	electrical resistance of a thermocouple
R	load resistance
m	ratio $\frac{R}{r}$
M	optimum ratio $\left(\frac{R}{r}\right)_{opt.}$
Z	figure of merit of a thermoelement, $\frac{\alpha^2}{k\rho}$
z	figure of merit of a thermoelement "pair", defined in Section 4 of the text
n	concentration of carrier electrons or "holes"
u	carrier mobility
e	electronic charge
W	electrical power delivered to load
I	current
V	voltage
E	generator open circuit voltage
N	number of thermocouples comprising a generator
S	surface area
L	length
K	lumped constant, defined in Section 4 of the text
Q	rate of dissipation of heat
T	temperature

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APPENDIX 1

OPTIMUM DESIGN FOR A 100 WATT 25 VOLT THERMOELECTRIC GENERATOR

It is assumed that materials which are known to exist and to have values of z of around $2.5 \times 10^{-3}/^{\circ}C$ will be suitable and available for fabrication into compact and optimised thermoelectric generators.

Let the 100 watts be supplied in the form of 4 amps at 25 volts, that is, given a load resistance of 6.25 ohms. Suppose a heat source is available to maintain the hot junctions of the generator at $T_1 = 500^{\circ}K$ and an infinite sink to maintain the cold junctions at $T_o = 300^{\circ}K$.

The optimum ratio of the load resistance R to the internal impedance r is given by:-

$$\left(\frac{R}{r}\right)_{opt} = M = \sqrt{1 + \frac{1}{2} z \, (T_1 + T_o)} = \sqrt{1 + \frac{400 \times 2.5}{10^3}} = 1.414.$$

The maximum efficiency attainable is

$$\eta_{max} = \frac{T_1 - T_o}{T_1} \times \frac{M - 1}{M + \frac{T_o}{T_1}}$$

$$= \frac{200}{500} \times \frac{0.414}{2.014} \times 100$$

$$= 8.22\%.$$

Now we have that the required output from the generator

$$E = I \, (R + r)$$

$$= IR\left(1 + \frac{1}{M}\right).$$

Since the voltage output from each couple is $\alpha \, (T_1 - T_o)$ the total number of couples required is $N = \dfrac{IR\left(1 + \frac{1}{M}\right)}{\alpha(T_1 - T_o)}$.

Assuming that the two thermoelectric materials have nearly optimum values for the thermoelectric power, namely $+200\ \mu V/^{\circ}C$ and $-200\ \mu V/^{\circ}C$ respectively, giving $\alpha = 400\ \mu V/^{\circ}C$, we obtain $N = 533$ and $r = R/M = 4.42$ ohms.

If L is the length and S the cross-sectional area of each thermoelement, we have that $r = 2N\rho \, \frac{L}{S}$, where ρ is the mean specific resistivity of the two thermoelectric materials, which is assumed to be 1.0×10^{-3} ohm cm.

Therefore we obtain that $\frac{L}{S} = \frac{4.42 \times 10^{+3}}{1066} = 4.15 \text{ cm}^{-1}$. Fig.4 shows the total surface area occupied by the hot junctions of the generator as a function of the length of the thermoelement arms. An allowance of 50% of the cross-sectional area of the thermoelements was made for the insulation between elements. The estimated weight of the generator is shown in Fig.5 as a function of temperature difference between hot and cold junctions, the figure of merit, and the length of the thermoelement arms. Considering a form of construction similar to that illustrated in Fig.3 the depth of the generator was assumed to be 20% longer than the lengths of the arms to allow for the metal links and insulation.

The overall density of the generator was taken to be 7.2 gm/cc. Table 1 below gives the number of thermocouples for each type of generator and also the dimensions of each thermoelement.

TABLE 1

Figure of merit z per $^{\circ}$C	Temperature difference $(T_1 - T_0)$ $^{\circ}$C	Number of thermocouples required N	Length of thermoelement arm cm	Cross-section of each thermoelement assumed square of side cm
1×10^{-3}	100	1790	0.3 1.0 2.0	0.32 0.58 0.82
	200	890	0.3 1.0 2.0	0.23 0.41 0.58
	300	590	0.3 1.0 2.0	0.18 0.34 0.48
2.5×10^{-3}	100	1080	0.3 1.0 2.0	0.38 0.69 0.97
	200	530	0.3 1.0 2.0	0.27 0.49 0.70
	300	350	0.3 1.0 2.0	0.22 0.41 0.57

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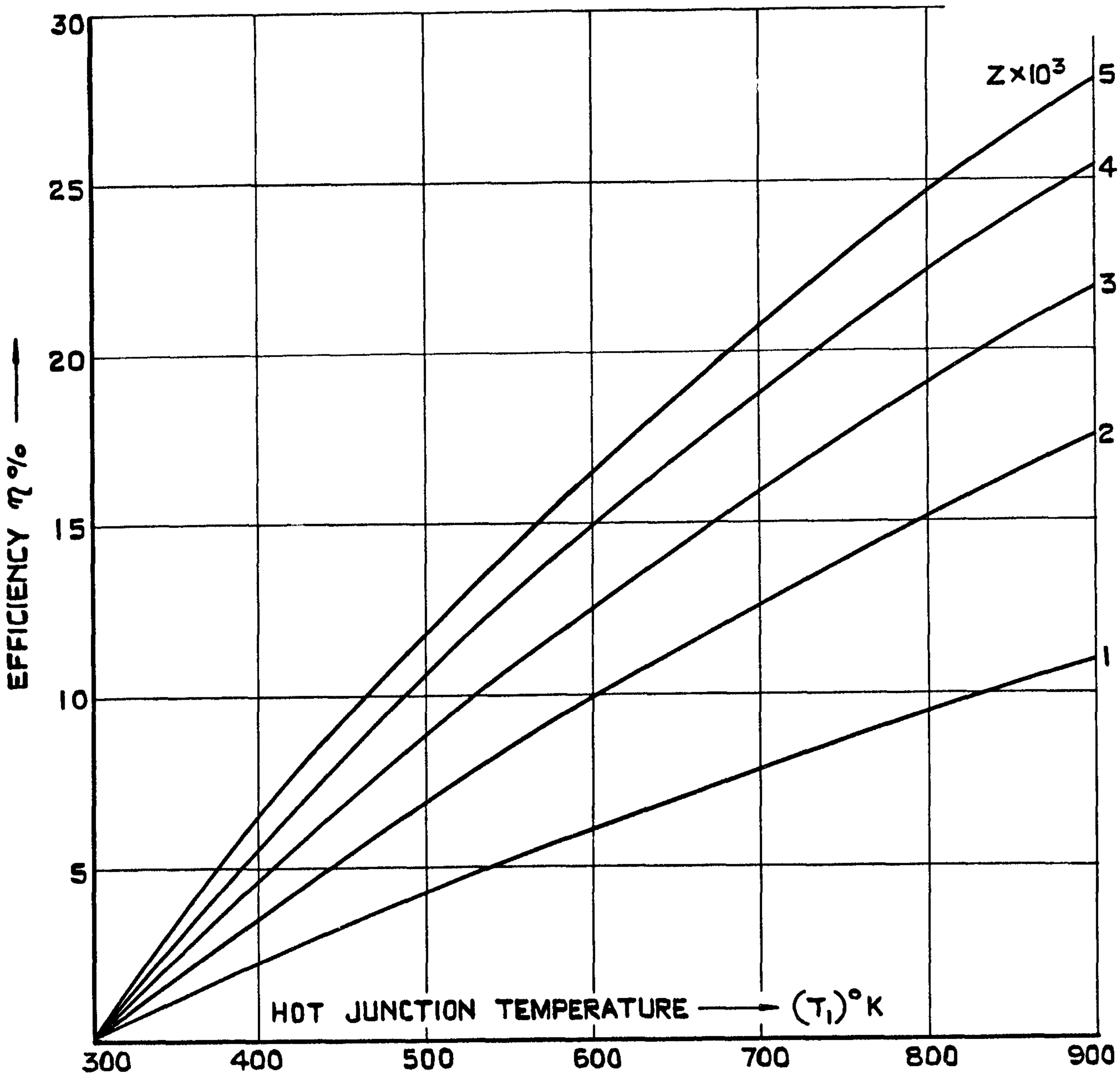

FIG.1 THE EFFECT OF HOT JUNCTION TEMPERATURE AND FIGURE OF MERIT ON THE EFFICIENCY OF THERMO-COUPLES.

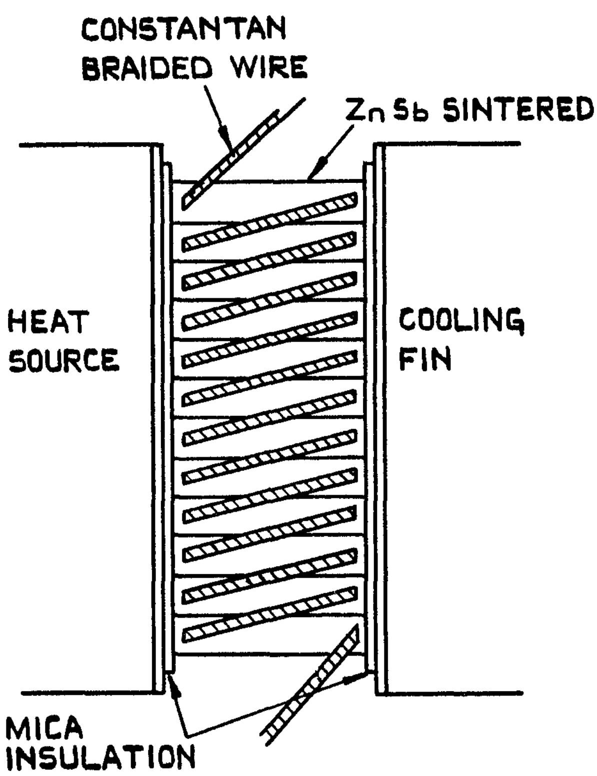

FIG.2 CONSTRUCTION OF THERMOELECTRIC GENERATOR

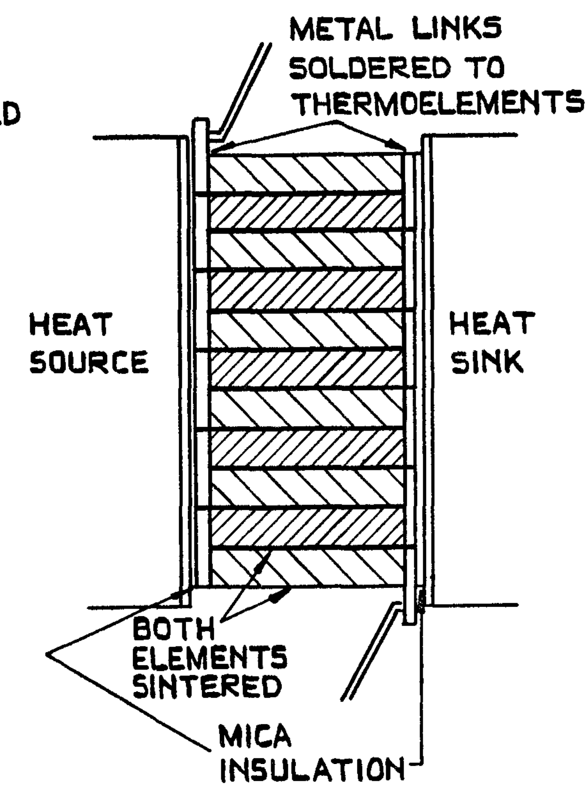

FIG.3 TYPICAL CONSTRUCTION FOR THE CASE OF BOTH THERMOELEMENT ARMS FORMED BY SINTERING.

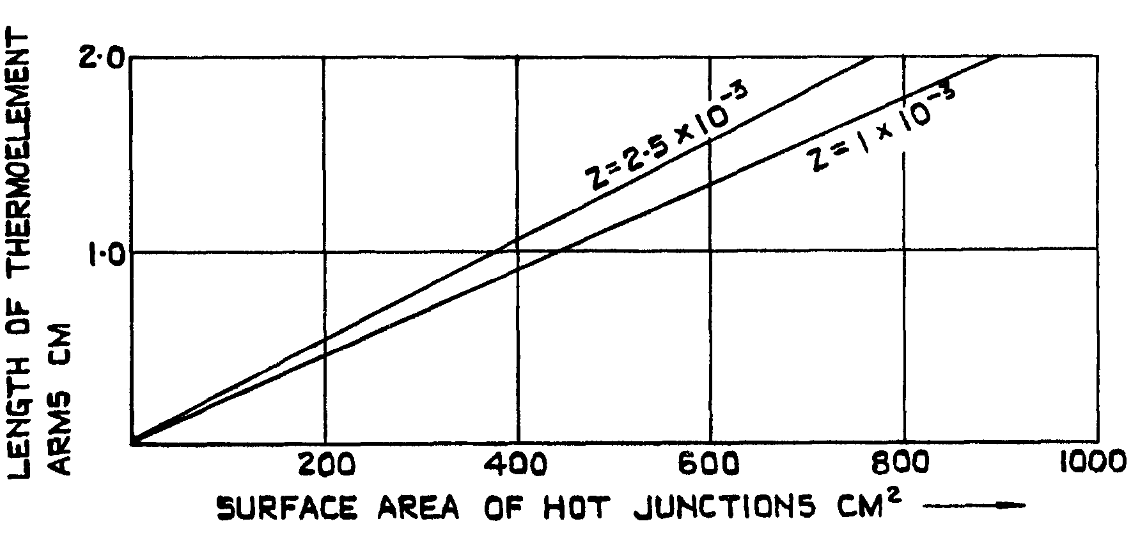

FIG. 4. OPTIMUM DIMENSIONS FOR A 100 WATT 25 VOLT THERMOELECTRIC GENERATOR WITH A TEMPERATURE DIFFERENCE ($T_1 - T_0$) OF 200°C.

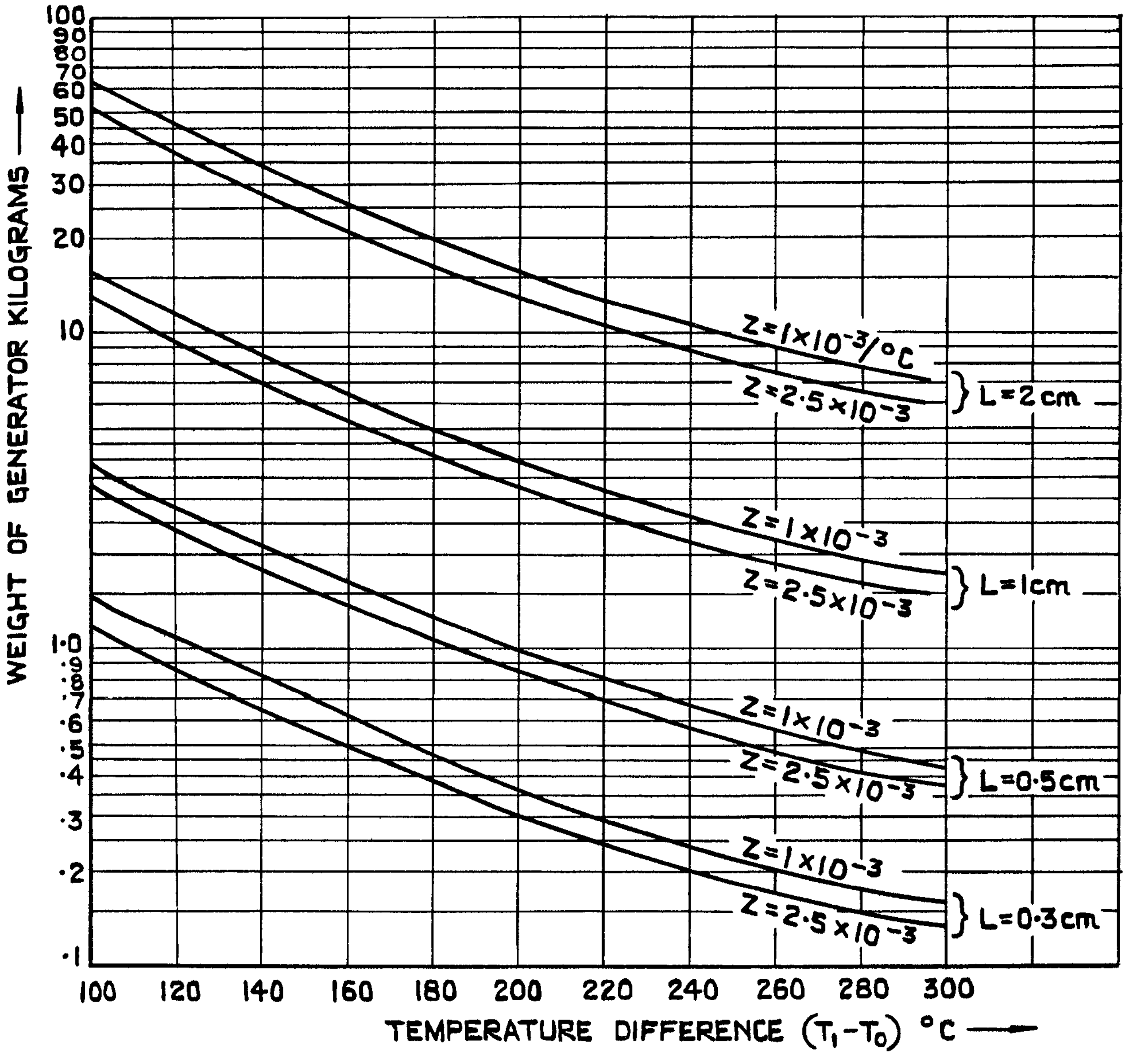

FIG. 5 DESIGN FEATURES OF A 100 WATT 25 VOLT THERMOELECTRIC GENERATOR.

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