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LEAD INDUSTRIES ASSOCIATION, INC.

292 MADISON AVENUE
NEW YORK 17, N. Y.

March 2, 1962

SUBJECT: THERMOELECTRIC MATERIALS

To Members of the Lead Industries Association, Inc.:

We are attaching an informative article on thermoelectric materials, which appeared in a recent issue of Materials in Design Engineering Magazine. It explains the possibilities of these materials and makes a good case for lead telluride. We believe you will find it interesting.

It is our plan to distribute the balance of our supply to people visiting our booth at the Design Engineering Show to be held in Chicago's McCormick Place, April 30 to May 3, 1962.

Very truly yours,

Executive Vice President

RLZ:mk
Enc.

Look Ahead with Lead

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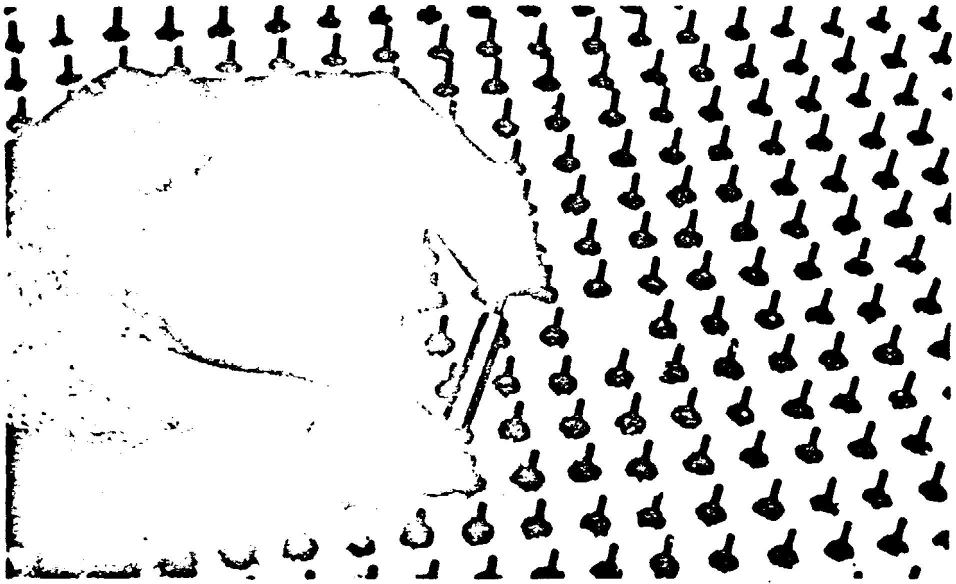

Lead telluride *elements turn heat from pilot flame into electric current needed to power control system for gas furnace*

Thermoelectric Materials Today

New and improved materials are bringing thermoelectric devices closer to commercial reality.

by Robert D. Carlton, *Thermoelectric Products Dept., Applied Research, Minnesota Mining & Mfg. Co.*

THERMOELECTRIC MATERIALS have the ability to 1) directly convert thermal energy into electrical energy, and 2) transfer thermal energy by means of an electric current. Although thermoelectricity is more than 100 years old, it was not until the 1940's with the advent of semiconductor technology, that its possible uses began to be realized. Recent materials advances have enabled engineers to come up with many unique and competitive devices for power generation and heat transfer.

Although several different materials are currently being used for generators, lead telluride (see Table 1) appears to be the best because of its high efficiency and its low cost. Germanium telluride exhibits slightly greater efficiency than p-type lead telluride, but when costs are considered the ratio of power to cost-per-pound is about one sixth that of lead telluride. Other compounds such as cesium sulfide can be operated at higher temperatures than lead telluride but their efficiencies are lower and material costs higher.

TABLE 1—PROPERTIES OF LEAD TELLURIDE ALLOYS

Density, lb/cu in.	0.294
Tensile Strength, psi	1,000+
Compressive Strength, psi	10,000+
Young's Modulus, psi	2×10^{6}
Coef of Ther Exp, per °F	10×10^{-6}

Most manufacturers have adopted bismuth telluride as a heat pump material. This is because bismuth telluride exhibits the most desirable thermoelectric properties between −50 and 400 F, the temperature range where heat pumps are most widely used.

Cost an important factor

Although thermoelectric devices have been successfully developed for many specialized applications, widespread commercial use can only be achieved if thermoelectricity becomes economically competitive with conventional systems. Thus, materials cost is an

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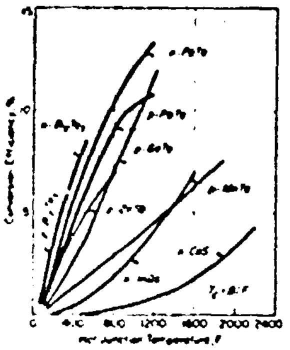
important design factor, as shown in Table 2 which compares the costs and efficiencies of thermoelectric generator materials.

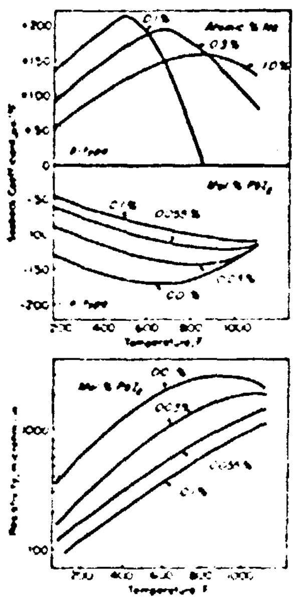
Note that the figures in the table reflect only the basic cost of the elements and do not include processing costs. Some of the materials are more difficult to process than others and this factor will affect the finished price of thermoelectric materials. However, on the basis of anticipated improvements in processing techniques, the dominant cost factor will be raw materials cost.

Temperature affects properties

The efficiency of the thermoelectric material is proportional to the temperature difference across it, whereas power is proportional to the square of temperature difference. This accounts for the fact that a material with low efficiency can still have a high power rating if it can be operated at a high enough temperature. Fig 1 shows how conversion efficiency of present thermoelectric generator materials varies with operating temperature. The end of each curve represents the highest temperature at which the material can maintain chemical stability.



1—*Conversion efficiency vs temperature for typical thermoelectric generator materials.*



2—*Effect of doping levels on properties of lead telluride.* TOP—*Seebeck coefficient vs temperature for lead telluride containing sodium and lead iodide doping agents.* BOTTOM—*resistivity vs temperature using lead iodide doping agent.*

Although efficiency values as high as 13% can be obtained with materials such as lead telluride, we must remember that these are theoretical efficiencies for converting thermal energy into electrical energy. In practice not all of the heat produced by the source flows through the thermoelectric material. Furthermore, resistance at contact points will detract from usable output power. Actually, the highest efficiency we have achieved in a practical device is 8.5%. This value represents true overall efficiency, i.e., the ratio of net electrical output to total thermal power input.

Theoretically, it is possible to obtain efficiency values as high as 18% by using continuous segments of different thermoelectric materials. By joining different materials in series electrically and thermally it is possible to use each material over the temperature range where it is most efficient. However, this procedure has its drawbacks, principally because care is needed to match the coefficient of expansion of various materials and because diffusion between the materials can cause degradation. Also, the technique is more costly and in practice has seldom produced more than a 10% increase in output.

TABLE 2—HOW THERMOELECTRIC MATERIALS COMPARE[a]

Material	Conductivity Type	Temp Diff (ΔT), °F[b]	Efficiency (N)[c]	Cost, $/lb[d]	Efficiency Cost Ratio	Power Cost Ratio
Lead Telluride (PbTe)	N	1080	13.5	5.92	2.28	25.8
	P	1080	11	5.92	1.86	19
Manganese Telluride (MnTe)	P	1800	7.8	20.72	0.38	5.7
Zinc Antimonide (ZnSb)	P	720	7.1	9.4	0.76	45
Bismuth Telluride (Bi_2Te_3)	N	450	8.7	9	0.97	4.4
Germanium Telluride (GeTe)	P	1115	12	47.56	0.25	3.02
Indium Arsenide (InAs) ...	N	1510	7.25	280	0.026	1.44
Bismuth Telluride (Bi_2Te_3)	P	1115	5.8	10.9	0.53	1.07
Cerium Sulfide (CeS)	N	2030	4.07	605	0.007	0.08

[a]Calculations based on use of materials in electrical generator. Values would be different if materials were used in heat pump.
[b]Greatest practical temperature difference consistent with material's chemical stability with cold junction maintained at 81 F.
[c]At cold junction temperature of 81 F. Efficiency = $S^2\Delta T/4K\rho$
[d]Based on production quantities.

How performance is measured

In addition to efficiency, the relative merit of thermoelectric materials is sometimes established by a "figure of merit":

$$Z = S^2/\rho K$$

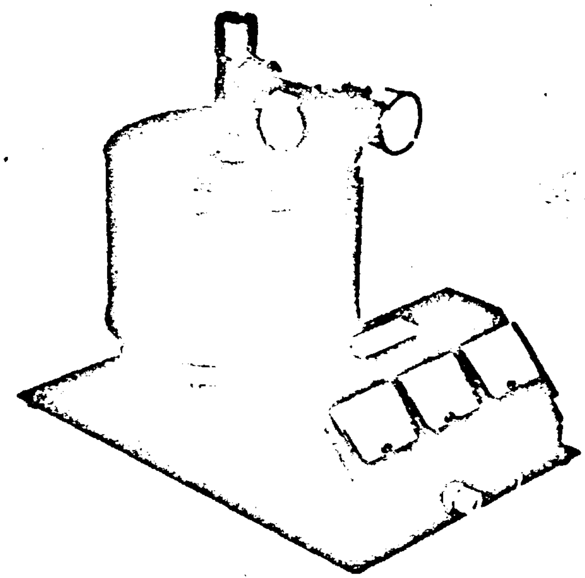
where S is Seebeck coefficient in μV/°C, ρ is electrical resistivity in μohm-cm, and K is thermal conductivity in w/cm °C.

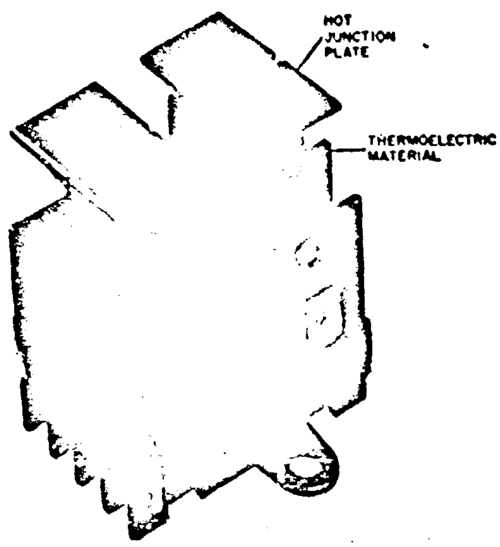
A high figure of merit indicates a good material for either a heat generator or a heat pump. Because the three properties in the equation are not completely independent, a compromise is usually necessary to achieve the highest figure of merit. Each of the properties is dependent on operating temperature. Although temperature dependency is not too important with heat pumps which usually operate over a small range of temperature difference (e.g., 125° F), it can be an important materials selection factor for thermoelectric generators where a temperature difference of 800 to 1000° F is not uncommon. A material that performs well over one temperature range may be completely unacceptable over another range.

Concentrated materials development in the past decade has produced dramatic increases in the figure of merit values for thermoelectric materials. As a result of this progress some rather extravagant predictions have been made for the future. Figure of merit values of 0.005 or 0.006 may be obtained with future materials, but we should not expect these as a certainty. At the present state of the art we should be realistic and expect normal progress in processing of present materials.

Three processing methods

Binary and ternary thermoelectric materials can usually be formed by casting, crystal growing or powder pressing techniques. The best method to use depends on cost and performance requirements. The compounds are somewhat more difficult to form than elemental semiconductor materials. Although reasonable purity levels must be maintained during processing, purity requirements are not as high as for germanium and silicon materials used in transistors and diodes. In general, the state of the art has progressed to the point where we can now easily produce a material that is chemically stable over its operating range and does not deteriorate with time. Because of their susceptibility to oxidation, most





Thermoelectric generators *use unique properties of materials to convert heat into electric power. Experimental gas fired generator above produces 10 w to provide power in remote areas where regular electricity would be difficult and costly to obtain. Thermoelectric modules such as four-element unit below can be combined to increase power. Heat absorbed at hot junction plates generates power in series-connected thermoelectric element.*

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How Thermoelectrics Work

The basic phenomena of thermoelectricity were discovered in the 19th century by Thomas Seebeck and Jean Peltier. Today's thermoelectric generators stem from the discovery by Seebeck in 1822 that when the junction of two dissimilar metals is heated, a voltage is produced across the open terminals which is proportional to the temperature difference between the open terminals and the heated junction.

Present day heat pumps stem from the discovery by Peltier a short time later that an electric current flowing across a junction of two dissimilar metals causes heat to be absorbed or evolved at the junction, depending on the direction of current flow.

Actually, thermoelectric generation and heat pumping are merely two aspects of the same phenomenon. Thermoelectric generation is an energy conversion process and heat pumping is an energy transfer process.

Thermoelectric generators and heat pumps usually operate with p-type and n-type materials. (Note: n-type materials have concentrations of electrons; p-type materials have concentrations of "holes" or locations devoid of electrons.) In a thermoelectric generator, the temperature gradient causes electrons in the n-type material and holes in the p-type material to move toward the cold ends, thus creating a potential difference. Conversely, in a heat pump, when an electric current is passed through a heat absorbing junction it is carried by electrons in the n-type material and holes in the p-type material. These charge carriers both move away from the junction and carry away thermal energy, thereby reducing temperature at the junction.

thermoelectric materials must be hermetically sealed if they are to be operated above 500 or 600 F.

Thermoelectric materials are usually more heavily doped than other semiconductor materials. The effect that doping has on properties is illustrated in Fig 2 which shows how an increase in doping level reduces both the resistivity and Seebeck coefficient of lead telluride. The proper amount of doping to use depends on the particular application. If a high emf and low power are needed, then a small amount of doping produces the best results. If power is more important, then heavy doping is often more suitable.

Many methods of contacting thermoelectric materials to their electrodes are in general use. Some of these are: casting the materials on to the electrode; soldering; and use of pressure contact. Each has its advantages, depending on the material involved and the application. Care is required when selecting an electrode material to prevent contamination. Certain metals, for example, will react with thermoelectric materials and degrade their properties or cause a high-resistance contact.

Current uses

The most important advantages of thermoelectric devices are their long life and maintenance-free operation. In addition to the novel devices shown in the photos, 3M engineers have also developed:

- An experimental electric generator for satellites and space vehicles which directly converts the heat of a radioactive isotope into electric power for communications
- A lighting system for buoys and other navigational equipment which eliminates battery systems by directly converting the energy from the combustion of natural gas into electrical energy
- Spot coolers located near the center of fluorescent lights which cool a small area on the wall of each lamp bulb, thus maintaining mercury vapor pressure at the optimum value and increasing light output by as much as 72%. ●●

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