
P. M. Solanki  
Assistant Professor, Mechanical Engineering, SSBT’s COET, Bambhori, (M. S.), India  
Email: p_msolanki@rediffmail.com

Dr. D.S. Deshmukh  
Professor & Head, Mechanical Engineering, SSBT’s COET, Bambhori, (M. S.), India  
Email: deshmukh.dheeraj@gmail.com

ABSTRACT: World from the last few years facing difficulties regarding energy management, energy consumption and sources of energy like renewable and non-renewable, are insufficient in comparison of the future energy trends. This is not only due to world population but also a long range of electrical and electronics based demands of modern life are responsible for it. These all causes the world that leads to the need of introduction of some techniques, modifications, nuclear power plants and nano cells to overcome the energy crisis. Thermoelectric modules playing an important role by the conversion of waste heat into electricity. The implementation of thermoelectric devices with cheap, single step power generation and without any pollution can be considered as key factors to green energy generations. In such regions the thermoelectric generators can be used to produce adequate amount of power like heat of stoves, wood, daily wastage. Such issues are also come into picture in engineering fields due to large scale consumption of energy and low efficiency of modern high facilitated devices. Attempts are also being made to improve the competitiveness of thermoelectric generators in directions other than by improving the figure-of-merit for materials. In particular, efforts are focused on increasing the electrical power factor, decreasing cost and developing environmental friendly materials. In addition to this the fuel cost is low or free as in waste heat recovery systems using thermoelectric generator. The cost per unit power generation is mainly determined by the power per unit area and operating period. Thus in this paper all desirable properties of good materials for thermoelectric generators are discussed.

KEYWORDS: Thermoelectric power generation, Waste-heat recovery, Alternative green technology, Direct energy conversion, Electrical power, Thermoelectric materials.

I. INTRODUCTION:

Thermoelectric (TE) devices create electricity from a thermal gradient or create a thermal gradient from electricity via the thermoelectric effect. This phenomenon comprises three related effects, uncovered as a series of discoveries made primarily by Thomas Johann Seebeck, Jean-Charles Peltier, and William Thomson (Lord Kelvin) in the 19th century[1]. The Seebeck effect asserts that a potential gradient will be created across a conducting material when one side of the material is hotter than the other. In reality, charge carriers (electrons and holes) in the material having higher thermal velocities on the hot side of the material naturally diffuse more quickly from the hot side to the cold side than in the opposite direction. If the thermal gradient across the material is maintained, flowing charge carriers build up on the cold side of the object, and this separation of charge creates a potential gradient which creates a potential difference between the two sides of the material which counts this charge imbalance. In the case that the material is part of a circuit, this voltage induces a current which be used to power a load [1]. Figure1 illustrated a conductor under a thermal gradient, charge carriers (electrons in this case) on the hot side have higher thermal velocities, diffusing more quickly to the cold side of the material than electrons on the cold side diffuse to the hot side. This leaves an excess of carriers on the cold side, and a potential gradient and electric field are created across the material[2] and essentially constitutes a conversion of thermal energy to electricity. The potential difference created per degree of temperature gradient across the material is its Seebeck coefficient, S, and is material-dependent [1].
The Seebeck effect’s complement is the Peltier effect which states that when current is applied to a conducting material, a temperature difference is induced between the sides of the material where current enters and exits [1]. Flowing charge carriers carry heat from one end of the material to the other, effectively cooling one side and heating the other. The heat transferred per unit of current applied is the Peltier coefficient, \( \Pi \), is also material dependent. Lord Kelvin later discovered that the Peltier coefficient is directly related to the Seebeck coefficient by the absolute temperature at which the quantities are measured. The Thomson effect describes the heating or cooling of a homogeneous conducting material due to current passing through it as a result of a thermal gradient [1].

The energy management (in its form of electricity) in the rural regions or icy areas is also a big deterrent in the daily life activities. In some of these areas the electric power is neither feasible to supply nor be economic for production.

II. THERMOELECTRIC DEVICES AND APPLICATIONS:

Thermoelectric devices have been created and commercialized from materials which are particularly efficient in converting thermal to electrical energy and vice versa. TE devices are useful for either generating power (by the Seebeck effect) or for localized heating and cooling (by the Peltier effect). Schematics of a typical thermoelectric device used in both ways are shown in Figure 2. This device is comprised of two semiconductor “legs,” one n-type (electrons) and one p-type (positively-charged holes), which are connected electrically in series and thermally in parallel. When a temperature difference is maintained between the top and bottom of the legs, holes and electrons flow from hot to cold, and both legs contribute to the current which powers a load (Figure 2a). On the other hand, when power is supplied to this circuit, heat is transferred by flowing electrons and holes from one side of the device to the other, creating a temperature difference at opposite ends of the device (Figure 2b).

Fig 1. Conversion of thermal energy to electricity under a thermal gradient [2].

Fig 2: Schematics of single elements of a typical thermoelectric device (a) a load is powered from a supplied temperature gradient for a Peltier cooler (b) a hot side and a cold side are created as a result of power applied to the device [7].
The practicality of their use is determined by cost-benefit analysis dependent on factors such as device efficiency, ease of integration, need for remote power generation, and cost of the heat source. Because current TPGs are not of particularly high efficiency (typically <5%) [1] and are often costly, they are generally only practical in locations where traditional power generation is not available, such as on spacecraft. However, if TPG efficiency increases, applications in transportation (e.g., in hybrid vehicles and submarines) and in peak power generation (e.g., using waste heat from nuclear and fossil fuel power plants and possibly in conjunction with solar panels) may become accessible.

III. THERMEOLECTRIC MATERIAL PROPERTIES:

There is a great deal of ongoing research in the TE field to improve material and device efficiency. The efficiency of the n- and p-type semiconducting materials comprising TE devices can be directly measured or calculated from important material properties which are individually measured. Thermoelectric materials are rated by a dimensionless figure of merit, ZT, where a higher ZT translates to higher efficiency. ZT is given by

\[ ZT = \frac{S^2 \sigma T}{k} \]

where S is the Seebeck Coefficient, \( \sigma \) is electrical conductivity, T is the temperature at which these properties are measured, and \( k \) is thermal conductivity.\(^1\) The electrical component of ZT, \( S \sigma \), is often considered separately and is dubbed the thermoelectric power factor. The thermoelectric properties defining ZT are not independent, however, and there is an important tradeoff between all of these traits. Indeed, a low thermal conductivity is desirable for higher ZT, yet thermal conductance depends on heat transfer by both phonons and electrons, so a high electrical conductivity yields a high thermal conductivity as well. This relationship is best described by the Wiedemann-Franz law, which equates the ratio of electronic contribution to thermal conductivity to electrical conductivity to a constant (the Lorenz number) times the temperature at which these properties are measured [1]

\[ LT = \frac{K e}{\sigma} \]

Furthermore, a high Seebeck coefficient necessitates a large charge separation in the material (i.e. more carriers on one side than the other), but a high electrical conductivity will cause quick and easy diffusion to negate this potential difference. High thermal conductivity also means difficulty in maintaining a high thermal gradient, also causing Seebeck coefficient to suffer. The majority of TE devices currently on the market utilize bulk semiconducting materials which are alloyed to reduce thermal conductivity, yielding ZT=1 near room temperature. In order for TE devices to be efficient enough to enter the power generation playing field, the efficiency of the semiconducting materials must increase dramatically and over a wide temperature range. A ZT of 2 would make TE devices viable for more niche applications and a ZT of 3 would allow TPGs to compete with traditional mechanical power generators [3].

IV. SIGNIFICANCE OF FIGURE OF MERIT (ZT):

Greater the value of ZT more will be the conversion efficiency of a thermoelectric material and vice versa. So it is clear that to improve the performance of a thermocouple the electrical conductivity should be increased and thermal conductivity should be reduced. Some researchers tend to improve ZT with different advanced methods like combination of suitable materials, palleting techniques and nano technology etc (Kantser et al., 2006; Bejenari et al., 2010; Kuei et al., 2004; Bilu et al., 2001). Generally, the phonon waves are responsible for the thermal conductivity, so to reduce it, the flow of phonons should face some interactions. The nano techniques; in which the nano size particles able to distort the oscillations of phonons that reduce the thermal conductivity and hence a significant improvement in the figure of merit which has been employed in the silicon nano wires successfully (Zheng, 2008). The figure of merit also studied for the oxygen deficient perovskites that determines their thermal and electrical properties and concluded to the enhancement of seebeck coefficient (Rodriguez et al., 2007; Brown et al., 2006; Jianlin et al., 2009; Mingo N., 2004; Bhandari et al., 1980; Micheal et al., 2008) and hence the thermo power generation. In this presented work we compare the experimental and theoretical values of the figure of merit (ZT) for some of the common thermoelectric materials like Cu, Fe, Constantan and Nichrome.

V. DEPENDENCES OF FIGURE OF MERIT (ZT):

It is clear that the figure of merit of a thermocouple is affected directly by the electrical conductivity but inversely by the thermal conductivity of the
thermoelectric material. (a) The thermal conductivity of a material is the ease with which the heat flows through itself and its expression from literature is given by:

\[ \lambda = \frac{\Delta Q}{\Delta t} \times \frac{1}{A} \times \frac{x}{\Delta T} \]

Where, \( \frac{\Delta Q}{\Delta t} \) is the rate of heat flow, \( \Delta T \) is the temperature gradient, \( A \) is the area of cross section of the thermoelectric materials with thickness \( x \).(b) The electrical conductivity of a thermoelectric material is the ease of the material to allow the passage of electric current and is given by

\[ \sigma = \frac{1}{\rho} = \frac{1}{RA} \]

Where \( R \) is the resistance of thermoelectric material in ohms, and \( R = \frac{\rho l}{A} \) where \( \rho \) is the resistivity (specific resistance) of the material in \( \Omega m \), \( l \) and \( A \) are the length and area of cross-section of the material respectively.

VI. THERMOELECTRIC POWER GENERATOR PERFORMANCE CALCULATION:

The performance of the thermoelectric calculation[8]

\[ Z = \frac{\alpha^2}{kR} \]

Where \( Z \) = Thermoelectric material figure of Merit
\( \alpha \) = See back Coefficient is given by
\( \alpha = -\frac{\Delta V}{\Delta T} \)
\( \Delta V = Voltage \ difference \)
\( \Delta T = temperature \ difference \)
\( R \) is the electric resistivity
\( K \) is the thermal conductivity

This figure of merit can be multiplied by \( T \) average absolute temperature of hot and cold plates of the thermoelectric module, \( K \)

\[ ZT = \alpha^2 T/kR \]

Here

\[ T = T_H + T_L/2 \]

Where \( T_H \) = Temperature at hot End
\( T_L \) = Temperature at cold end

See back Coefficient

\[ \alpha = -\frac{\Delta V}{\Delta T} \]

By the second law of thermodynamics, the ideal (absolute maximum efficiency of the thermoelectric power generator operating as a reversible heat engine is Carnot efficiency

\[ \eta = \frac{W_e}{Q_H} \]

\[ \eta_{max} = 1-T_L/T_H \]

The maximum conversion efficiency of an irreversible power generator can be estimated using

\[ \eta = \eta_{carnot} \left[ \frac{\sqrt{1+ZT} - 1}{\sqrt{1+ZT} + TL/TH} \right] \]

VII. THERMOELECTRIC MATERIALS FOR POWER GENERATORS:

Among the vast number of materials known to date, only a relatively few are identified as thermoelectric materials. As reported by Rowe [4], thermoelectric materials can be categorized into established (conventional) and new (novel) materials. Today’s most thermoelectric materials, such as Bismuth Telluride (Bi\(_2\)Te\(_3\)) -based alloys and PbTe-based alloys, have a \( ZT \) value of around unity (at room temperature for Bi\(_2\)Te\(_3\) and 500-700K for PbTe). However, at a \( ZT \) of 2-3 range, thermoelectric power generators would become competitive with other power generation systems. The figure-of-merit \( Z \) of a number of thermoelectric materials together
Effective thermoelectric materials should have a low thermal conductivity but a high electrical conductivity. A large amount of research in thermoelectric materials has focused on increasing the Seebeck coefficient and reducing the thermal conductivity, especially by manipulating the nanostructure of the thermoelectric materials. Because the thermal and electrical conductivity correlate with the charge carriers, new means must be introduced in order to reconcile the contradiction between high electrical conductivity and low thermal conductivity as indicated by Weiling and Shantung [5].

VIII. CONVENTIONAL THERMOELECTRIC MATERIALS:
Rowe [4] reported that established thermoelectric materials (those which are employed in commercial applications) can be conveniently divided into three groupings based on the temperature range of operation, as shown in Fig. (4). Alloys based on Bismuth (Bi) in combinations with Antimony (Sb), Tellurium (Te) or Selenium (Se) are referred to as low temperature materials and can be used at temperatures up to around 450K. The intermediate temperature range - up to around 850K is the regime of materials based on alloys of Lead (Pb) while thermo elements employed at the highest temperatures are fabricated from SiGe alloys and operate up to 1300K. Although the above mentioned materials still remain the cornerstone for commercial and potential power generating applications relevant to waste heat energy is shown in Fig. (4).[4] Effective thermoelectric materials should have a low thermal conductivity but a high electrical conductivity. A large amount of research in thermoelectric materials has focused on increasing the Seebeck coefficient and reducing the thermal conductivity, especially by manipulating the nanostructure of the thermoelectric materials. Because the thermal and electrical conductivity correlate with the charge carriers, new means must be introduced in order to reconcile the contradiction between high electrical conductivity and low thermal conductivity as indicated by Weiling and Shantung [5].
IX. NOVEL THERMOELECTRIC MATERIALS & MODULE CONFIGURATION:

It was recently reported in [6] that a material which is a promising candidate to fill the temperature range in the ZT spectrum between those based on Bi₂Te₃ and PbTe is the semiconductor compound β-Zn₃Sb₄. This material possesses an exceptionally low thermal conductivity and exhibits a maximum ZT of 1.3 at a temperature of 670K. This material is also relatively inexpensive and stable up to this temperature in a vacuum [6]. Another recent direction to improve the competitiveness of thermoelectric materials, other than by improving the figure-of-merit, is by developing novel thermoelectric module shapes.

X. CONCLUSION:

Study of thermoelectric materials selection criteria indicates that efficiency of the thermoelectric generator depends upon the figure of merit for materials, is key consideration for comparing the efficiency of thermoelectric materials. It is observed that most commonly used thermoelectric materials, are Cu, Fe, Constantan and Nichrome, Bismuth Telluride (Bi₂Te₃)-based alloys and Lead Telluride (PbTe)-based alloys. Effective thermoelectric materials should have a low thermal conductivity but a high electrical conductivity. A lot of research in thermoelectric materials is focused on increasing the Seebeck coefficient and reducing the thermal conductivity, especially by manipulating nanostructure of thermoelectric materials.

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