The CrSi₂-CoSi Thermomodule and its Applications

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The purity of the starting metals required for the preparation of a thermomodule composed of $CrSi_2$ and CoSi was examined. It was found that 99% grade is good enough for practical use. By means of direct hot-pressing, laminated plates with alternate layers of $CrSi_2$ and CoSi were prepared; these were then cut to give U- or W-shaped modules. The thermoelectric performance and durability of the modules was examined. It was found that direct exposure to the reducing town gas flame led to the destruction of the n-branch CoSi, and several methods of protection against the corrosive gas flame were devised and tested. Moreover $Cr_{0.6}Mn_{0.4}Si_{1.88}$ and $TiSi_2$ were put forward as new n-branch material. Some trial models of a thermogenerator are also described.

1. Introduction

Various metallic thermocouples are widely used as sensing elements for temperature measurement. In recent years, new materials have been developed and used as thermoelectric conversion elements for generating electric power [1–6] or for refrigeration [7–9]. To distinguish them from normal thermocouples, elements for thermoelectric energy conversion have been called *thermomodules.*

Generally speaking, normal thermocouples are made of a pair of metallic wires, while in thermomodules one uses semiconductor materials. Thermoelectric energy conversion is, in general, not advantageous in respect of its efficiency. However, advantages are found in some cases to compensate for the low efficiency: for example, a low voltage and heavy current DC source with superior characteristics, the utilisation of low-grade heat from a heat source (applications of which are dealt with in this report) and the utilisation of nuclear energy are realised by use of thermomodules [10–14].

As a thermomodule is considered to be a heat engine which works between a high temperature heat source T_1 and a low temperature heat sink

T_0, the efficiency, η is given by [15]

$$\eta = [(T_1 - T_0)/T_1][(M - 1)/(M + T_0/T_1)] \quad (1)$$

$$M = \sqrt{1 + Z(T_1 + T_0)/2} \quad (2)$$

where Z is called the *figure of merit* of the thermomodule. When its thermoelectric power, electrical conductivity and thermal conductivity are α, σ and κ, respectively, Z is defined by

$$Z = \alpha^2 \sigma / \kappa$$

The first factor in equation 1 represents the efficiency of Carnot's cycle. The second factor, which is always smaller than the first, shows that the efficiency decreases owing to the irreversible processes (thermal conduction and Joule heat). Equation 1 shows, moreover, that with increase in the figure of merit, Z, and the average working temperature, $(T_1 + T_0)/2$, η approaches the thermodynamic value, $(T_1 - T_0)/T_1$. Consequently, materials for thermomodules have been developed and studied along the following lines: to find materials with a superior heat- (and corrosion-) resistance (in order to raise the average working temperature) and at the same time with Z as large as possible. The former is

connected with research on heat-resisting ceramics, cermets and special intermetallic compounds, whilst the latter with the investigation of refractory semiconducting materials. It has been reported by the present authors that a chromium disilicide/cobalt monosilicide couple, $CrSi_2$–$CoSi$ is one of the most promising thermomodules [3, 4, 16].

Z-values have been measured as $Z_{CrSi_2} = 2.83 \times 10^{-4}$ deg^{-1} and $Z_{CoSi} = 0.85 \times 10^{-4}$ deg^{-1} at room temperature [4, 6] respectively. These values lie between 3×10^{-3} deg^{-1} (for the most superior chalcogen compound thermoelement, such as Bi_2Te_3 [7, 9] and 2×10^{-5} deg^{-1} for a representative metallic thermocouple element (such as alumel or chromel). $CrSi_2$–$CoSi$, as a high temperature thermomodule, ought to be superior in efficiency to the above-mentioned chalcogen compound when it operates at a temperature as high as 1300° K. This is due to the fact that $(T_1 - T_0)/T_1$, in equation 1, becomes the factor of primary importance in high-temperature uses.

The purpose of the present study was mainly to examine the performance and durability of the module, $CrSi_2$–$CoSi$, but also to develop the field of its application.

2. Preparation of Specimens

Low purity powders of $CrSi_2$ and $CoSi$ were prepared by a procedure described already in the literature [16]. The high purity powders were prepared from mixed powders (silicon and the respective metal) by a solid state reaction in a sealed quartz tube at a temperature of 1000 to 1200° C. Identification was effected by X-ray analysis. The powder was hot-pressed into a plate, out of which a rectangular parallelepiped specimen $15 \times 15 \times 2$ mm³ was cut. The thermomodule, the mechanically coupled $CrSi_2$–$CoSi$, was prepared by the simultaneous hot-pressing of $CrSi_2$ and $CoSi$ powders into a laminated biplate. Then, a part of the boundary of the biplate was cut out leaving one end as it was to give a U-shaped junction. In much the same way, W-shaped junctions were also prepared (fig. 1a). The boundary cutting could be eliminated by preparing a laminated plate incorporating an insulator: $CrSi_2$–Mg_2SiO_4–$CoSi$–Mg_2SiO_4–$CrSi_2$– . . .

Electron-probe microanalysis showed that the mutual diffusion range never exceeds 3 μm (the diameter of the beam spot) from the boundary (fig. 1b). The mechanical strength of the junction thus prepared is given in table I. In order to ensure good electrical and thermal contact with the output terminal, the two ends of the module were electroplated with Ni or Pd and then plated with Sn–Pb alloy.

The purity of the starting metals was of the following grade: Si 98%, Cr 99% and Co 99% for the low purity silicides and Si 99.999%, Cr 99.99% and Co 99.9% for the high purity silicides.
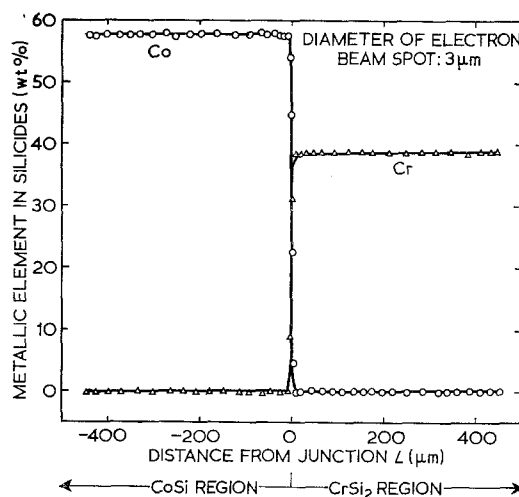
3. Experimental Results
3.1. Thermoelectric Properties

The method of measurement has been described in the literature [17]. The temperature-depend-
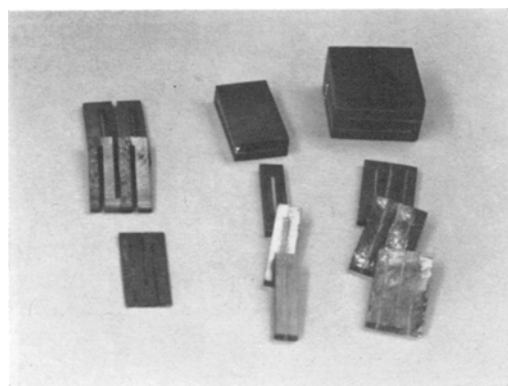
(a)

(b)

Figure 1 (a) Some $CrSi_2$–$CoSi$ modules. (b) Electron-probe microanalysis for the hot-pressed boundary of $CrSi_2$–$CoSi$.

TABLE I The mechanical strength of the junction CrSi$_2$-CoSi

Method of preparation	Sintering condition	Modulus of rupture (kg/mm^2)
Cold-pressing	1200° C, 8 h, in Ar	14–15
Slip-casting [10]	1250° C, 6 h, in Ar	18–23
Hot-pressing	1250° C, 8 min, in Ar	26–27

ence of the thermoelectric power and electrical resistivity of CrSi$_2$ and CoSi with two different grades of the purity are shown in fig. 2. As is seen, the thermoelectric power and electrical resistivity for the high purity CrSi$_2$ (α_1 and ρ_1, respectively) are larger in comparison with those for the low purity one (α_2 and ρ_2, respectively) below 800° K. Intrinsic behaviour (independent of the purity) is seen above this temperature [3].
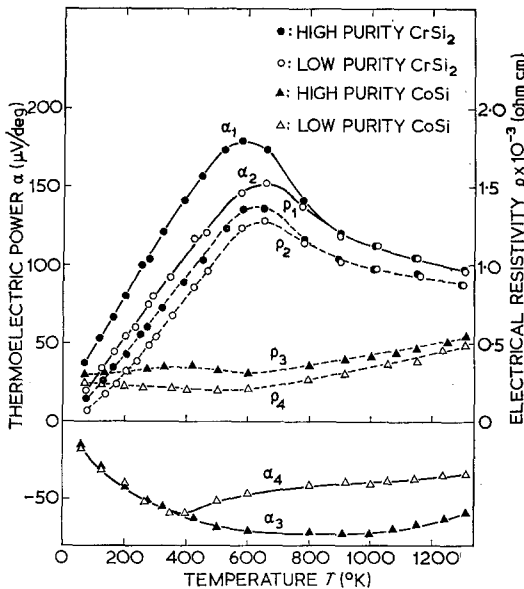

Figure 2 Effect of purity on thermoelectric properties for CrSi$_2$ and CoSi, respectively.

On the other hand, for CoSi, α_3 and α_4 as well as ρ_3 and ρ_4 show semi-metallic behaviour and intrinsic behaviour is not observed, at least up to 1200° K [5]. Corresponding Z values are estimated to be $Z_1 = 2.86 \times 10^{-4}$ deg^{-1}, $Z_2 = 2.33 \times 10^{-4}$ deg^{-1}, $Z_3 = 0.85 \times 10^{-4}$ deg^{-1} and $Z_4 = 1.15 \times 10^{-4}$ deg^{-1} at room temperature, using the measured values of the thermal conductivity, $\kappa_1 = 0.66$ watts deg^{-1} cm^{-1} and $\kappa_2 = 0.11$ watts deg^{-1} cm^{-1}. If the temperature variation of the thermal conductivity is ignored,

the variation in η between the low and the high purity modules operating between fixed temperatures, $T_1 = 300°$ K and $T_0 = 1200°$ K, is estimated to be 3 %. Such a degree of variation in η is well within that due to the variation in working temperature in practical use. Therefore, ordinary reagent grade metals are good enough for the preparation of the practical thermomodule.

3.2. Corrosion Test

Town gas or LPG was used as the heat source for the corrosion test at high temperatures. These contain H$_2$, S, C and water vapour. It was observed that CoSi, the n-branch of the module, is apt to dissociate in the reducing flame which contains water vapour, and fine powders of a black compound precipitate on the surface. On the other hand, CrSi$_2$, the p-branch, is fairly stable against such a flame except that the surface turns slightly greenish [18]. This poses the problem of improvement of the corrosion resistance of the n-branch against the gas flame. The improvement was carried out as follows: use of a suitable protecting cap; pretreatment of CoSi and development of new materials as will be described in section 3.

3.2.1. Protecting Cap

The thermomodule to be tested was mounted in the apparatus shown in fig. 3. The test was carried out both by continuous heating in a town gas flame at 1200° C for 5000 h and by giving 1000 thermal shocks (alternations of 5 min heating and 5 min cooling). Results are summarised in table II. As is seen, durability is best when the module is entirely covered with stain-
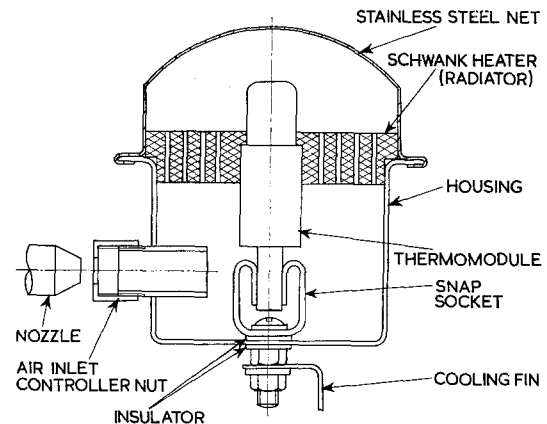

Figure 3 Apparatus for durability test.

TABLE II The life time of the modules with and without various forms of protection against the town gas flame at 1200° C.

No. of specimen	Protection	Life time (h)
1	without protection	48–160
2	with alumina and water-glass	10–50
3	with commercial alumina cement	120–600
4	with iron mesh and alumina cement	500–900
5	with iron cap cemented by alumina	1000–1500
6	with iron upper cap and stainless steel lower sleeve cemented by alumina, respectively	1000–1500
7	with iron upper cap and stainless steel lower sleeve cemented by graphite-alumina mixed powder (graphite rich for the former and pure alumina for the later)	1800–2000
8	with chromium plated upper cap cemented by graphite-alumina mixed powder (see fig. 4)	5000

less steel. However, because of its poor thermal conductivity, the effective temperature difference across the module is not satisfactory at all. Moreover, it is difficult to make such a press-formed cap suitable for mass production.

Therefore the cap was divided into two parts: the upper cap was made of a chromium-plated steel and the lower sleeve made of a stainless steel, as shown in fig. 4. Commercial alumina cement powder mixed with 30 to 50 wt % of graphite powder, was used as a cement for the upper cap and the pure alumina cement for the lower sleeve. The thermal conductivity is influenced by the composition of the cementing
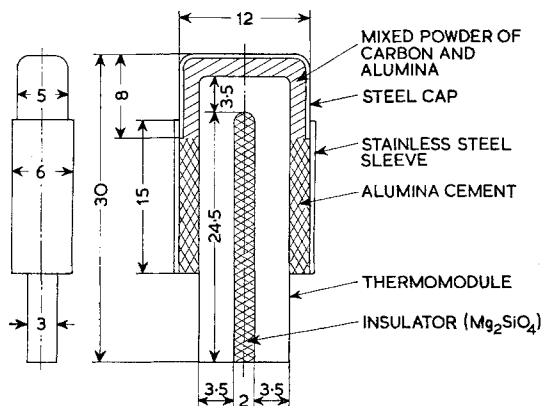

Figure 4 Section of thermomodule with corrosion protection.

materials. It increases with increase in the proportion of the graphite, which moreover prevents oxidation. By this method, the temperature at the junction of the module was raised to 800° C, as compared to 500° C when entirely covered with stainless steel. Accordingly, the thermoelectromotive force of the module increased from 60 to 110 mV. The change of the thermoelectromotive force and internal resistance are shown as a function of heating time in fig. 5. The size of the sample used is illustrated in fig. 4.
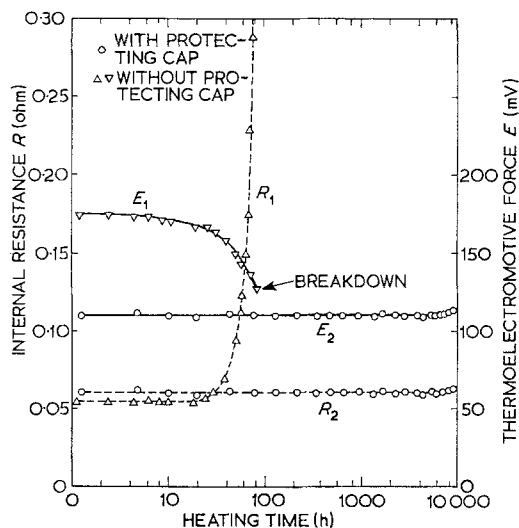

Figure 5 Change of thermoelectromotive force and internal resistance as a function of heating time. Cold junction, 25° C; hot junction, 1200° C; atmosphere, reducing gas flame.

3.2.2. Pretreatment

It was found that the corrosion resistance of CoSi is conspicuously increased by prior heat-treatment at 1100° C for about 160 h in air. When CoSi with a polished surface is exposed directly to a reducing gas flame, its weight and apparent volume increase with time, as shown by the curve 1 in fig. 6; this implies that a complex chemical reaction between CoSi and the gas flame proceeds with time. It was noticed that the weight change is remarkably reduced by prior heat-treatment in air (curve 2). In this case, the specimen was neither deformed nor destroyed even after heating in the reducing gas flame for 160 h. The explanation may be that a glass-like complex silicate layer might be formed on the surface of the CoSi by the preheating in the oxidising atmosphere and such a layer might to
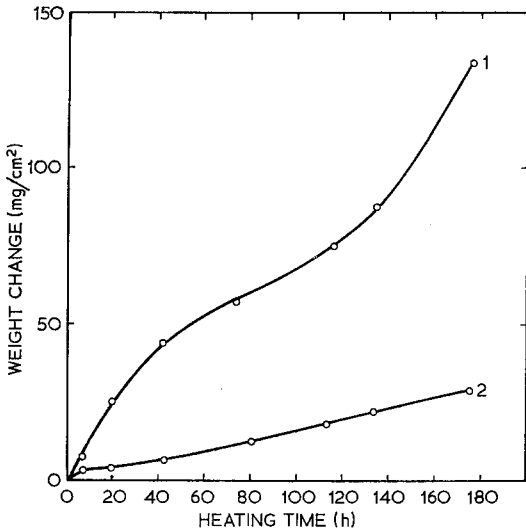
Figure 6 Weight change of CoSi with time in the reducing gas flame at 1200° C. 1, polished surface; 2, pre-oxidised surface.

some extent protect the CoSi from direct contact with the gas flame. However, the layer might not be sufficiently strong to prevent the gradual reaction of the CoSi with the reducing flame at temperatures above 1100° C.

3.3. Development of New Materials for the *n*-Branch

This was carried out in two ways; one was to convert the *p*-type $CrSi_2$ into an *n*-type alloy, because $CrSi_2$ is resistant to heat and corrosion; the other was to lower the absolute value of the thermoelectromotive force of $TiSi_2$ which is known as one of the good heat-resisting silicides [18–20] and has a very small positive value of thermoelectromotive force.

3.3.1. $Cr_{0.6}Mn_{0.4}Si_{1.88}$

According to structural and thermoelectric data, alloys with $CrSi_2$-type structure appear in the system $(1 - x)$ $CrSi_2 + xMnSi_2$, within $0 \leqq x \leqq 0.3$; at $x = 0.3$, α shows a minimum (positive) value, while ρ is a maximum [3]. Several authors have mentioned that manganese disilicide exists, in reality, in the form, $MnSi_{1.72}$ [21–24]. Therefore its thermoelectric properties were re-examined for the system $(1 - x) CrSi_2 + xMnSi_{1.72}$. Fig. 7 shows α and ρ at room temperature as a function of composition, x. It is seen that α changes abruptly from a large positive value ($+ 130 \mu V/° C$) to a large negative value ($- 120 \mu V/° C$) with increasing x from

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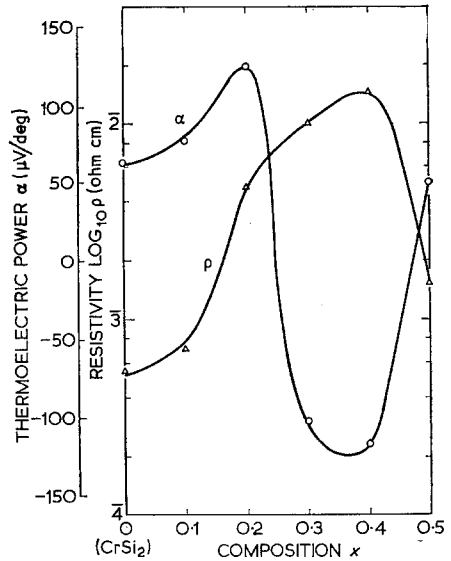0.2 to 0.3. The temperature-dependence of α is shown in fig. 8 for $x = 0.2$ and 0.4. As is seen,

Figure 7 Thermoelectric power and resistivity at room temperature for $(1 - x)CrSi_2 + x MnSi_{1.72}$.

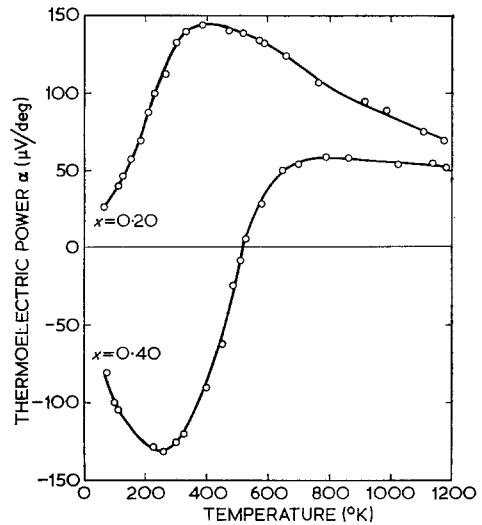*Figure 8* Temperature dependence of thermoelectric power for $x = 0.2$ and 0.4 in $(1 - x) CrSi_2 + x MnSi_{1.72}$.

the sign of α changes from minus to plus at a temperature which is higher for larger x. These observations indicate the possibility of $Cr_{0.6}$ $Mn_{0.4}Si_{1.88}$ as a new *n*-branch element. The thermoelectromotive force of several modules including $CrSi_2$–$Cr_{0.6}Mn_{0.4}Si_{1.88}$ is shown in fig.9
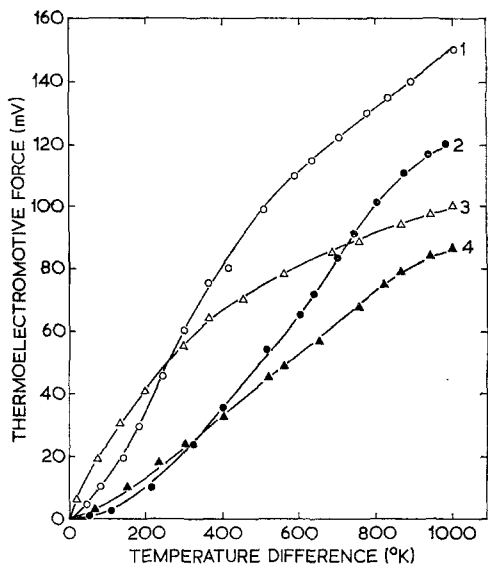
Figure 9 Thermoelectric force of modules composed of CrSi₂ and various n-branch materials. 1: CrSi₂–CoSi (high purity); 2: CrSi₂–CoSi with protecting cap; 3: CrSi₂–Cr₀.₆Mn₀.₄Si₁.₈₈; 4: CrSi₂–TiSi₂.

as a function of temperature difference. The performance is obviously inferior to the module, CrSi₂–CoSi. However, it is promising because of its low cost.

3.3.2. TiSi₂

The electrical properties of TiSi₂ are metallic: $\rho = 30 \times 10^{-6}$ ohm cm and $\alpha = +1.8\ \mu V/^\circ$ C at room temperature. Therefore, the thermo-electromotive force of a thermomodule which employs TiSi₂ as the n-branch is 2 to 3 times as large as that of CrSi₂–CoSi at the same temperature difference, as shown in fig. 9. However, there is no need to use a protecting cap against the corrosive gas flame in this case. Consequently the effective temperature difference becomes larger and it becomes possible to use TiSi₂ as the new n-branch material. Practically, it is impossible to join TiSi₂ directly with CrSi₂ by the method of hot-pressing mentioned above. However, by the addition of 1 mol % of FeSi₂ to TiSi₂, the above method becomes applicable in this case as well.

4. Some Applications

For the construction of apparatus using thermomodules the following precautions were taken: electrical matching of the internal resistance of the module to the load resistance, by selection of the size and form of the module, and release of thermal stress, by a flexible mounting of the module.

4.1. Thermogenerator for Teaching Demonstration

This thermogenerator is operated by an oil burner. Twenty-four thermomodules are connected electrically in series with each other and thermally in parallel, and mounted on copper electrodes each of which is equipped with a cooling fin. In the operating condition the temperature of the hot junctions $\sim 970^\circ$ C, while that of cold ones $\sim 140^\circ$ C, and the output voltage amounted to 3.2 V. The output power obtainable is shown by the curve 1 in fig. 10 as a function of temperature difference.
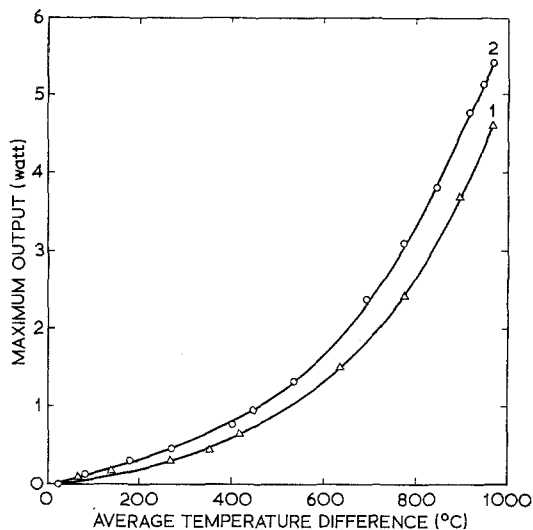

Figure 10 Maximum output power versus average temperature difference for trial thermogenerator. 1, U-shaped module ($\times$ 24); 2, W-shaped module ($\times$ 12).

4.2. Hot Air Circulator for Gas Stove

The thermogenerator used in this model is composed of 12 W-shaped thermomodules (as in fig. 1). The size of each branch is $3 \times 13 \times 30$ mm³. The output power is shown by curve 2 in fig. 10. The operation is as follows. Town gas heats a skeleton in which are arranged the hot junctions of each module. The heat energy gathered by the skeleton warms the surrounding air and at the same time, a part of the heat energy is converted by the modules to electric

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energy. A fan driven by the generator propels the hot air.

4.3. Safety Valve for Gas Equipment

The combination of a magnetic valve and thermogenerator composed of twelve pairs of metallic thermocouples is already available as an actuator for a safety and control valve [25]. By substituting a thermomodule for the metallic thermocouples, the construction of the magnetic valve may be simplified because of the strikingly large power available. A burner equipped with a safety valve of this type was constructed. The pilot burner and thermomodule are as shown in fig. 4. The magnetic valve used has an attractive force of 3 kg when the output power of the module is 100 mV, 200 mA.

5. Conclusion

The thermomodule, $CrSi_2$–$CoSi$, proved to have good thermoelectric properties and it has found some practical applications. The n-branch, $CoSi$, is, however, inferior to the p-branch, $CrSi_2$, in heat and corrosion resistance against the town gas flame. The difficulty has been avoided by use of a protecting cap and by means of prior heat-treatment of $CoSi$ in the air. A search for the new n-branch material has shown that $Cr_{0.6}Mn_{0.4}Si_{1.88}$ and $TiSi_2$ might be promising.

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