Modeling Temperature Gradient Evolution of CoSb₃ Material for Thermoelectric Devices during Spark Plasma Sintering

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The temperature distribution and evolution of Mo/Ti/CoSb₃ materials used as thermoelectric couples of devices during spark plasma sintering were simulated by finite element method, and the results agree well with the die interior temperature measured by thermocouple. The sample and punches have higher temperature in whole sintering process, the highest temperature region is existed in CoSb₃ region, and the radial temperature gradient in CoSb₃ region is obvious. It was confirmed by experiments that the temperature gradient in sample results in non-uniform microstructure and thermal conductivity difference. The temperature gradient increases with decreasing thermal conductivity and increasing electrical resistivity of CoSb₃-based compound, from the point of view of the thermal conductivity and electrical resistivity, respectively, the optimization method of the combined mechanical property and thermoelectric property of CoSb₃-based compound was proposed.

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1. Introduction

Spark plasma sintering (SPS) technique, also known as field activated sintering, employs pulsed direct current (DC) passing through a graphite die containing the sample to intensify sintering, the samples are sintered by Joule's heat generated in the sintered material and transferred from the graphite dies and punches. In the SPS process, the pulsed electric current flows through the sintered conduction material, and generates spark plasma at particle contacts, which creates a local high-temperature state for an extremely short time and causes evaporation of the powder surface, leading to the formation of the necks. However, the high-temperature state is localized on the surface of particles, and the neck can then be cooled due to thermal diffusion during the off state of the pulse. By applying the repeated on-off current, the local high-temperature field moves throughout the sample, and the temperature within particles tends to become uniform, the temperature gradients in sample significantly decrease. The general advantages of field assisted sintering, compared to traditional hot pressing or hot isostatic pressing are lower sintering temperature, shorter processing time, and higher heating rates thereby minimizing grain growth, which improves material property to a certain extent.¹⁻³⁾ Although these characteristics brought growing interest and widespread use of SPS technique, further research indicated that high heating rates, especially in combination with short dwell times, could cause temperature gradients in sample, and subsequently sintering inhomogeneity led to non-uniform microstructure, including grain size, etc, finally might appear mechanical properties difference in the sintered sample. Therefore, the temperature field within the sample during SPS process should be understood and

controlled to the best of our abilities.^{4,5)} Recently, there have been some works in simulating temperature distribution of sample during SPS process, including conducting and insulating materials.^{1,4,6,7)} However, for semi-conducting material used as thermoelectric (TE) devices, the thermoelectric property is sensitive to temperature, and mechanical property is relevant with temperature distribution in sample, thus it is necessary to study the temperature distribution and evolution of semi-conducting material during Spark Plasma Sintering.

TE devices have attracted a great deal of attention because of their application in solid state power generation using exhaust or waste heat sources.⁸⁾ Efficiency of TE device is highly dependent on the figure of merit of the TE material and temperature difference across the device. Recently CoSb₃-based skutterudite compound is regarded as one of the most promising materials to construct TE device working at intermediate temperature region (500–800°C), because of its relatively low thermal conductivity and high electrical conductivity.^{9,10)} However, as the key technology for fabricating TE device, the joining of metal electrode and CoSb₃ material is still a difficult problem. Nowadays, molybdenum (Mo) disk is chosen as electrodes due to its high electrical conductivity and thermal conductivity, and thermal expansion coefficient closing to that of CoSb₃.¹⁰⁾ And considering the difference in order of magnitude of thermal conductivity and electrical conductivity between CoSb₃ and Mo, Ti is applied as the transition layer since its thermal conductivity and electrical conductivity are intermediate between those of CoSb₃ and Mo. CoSb₃ powder, Ti powder and Mo disk electrode have been simultaneously sintered by SPS technique, in which the uniform temperature distribution is important for uniform microstructure and mechanical properties of Mo/Ti/CoSb₃ sample for the long-term use in power generation. However, there are few reports

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Table 1 Peak value of pulsed current vs. time during SPS process.

Time (sec)	0–60	60–120	120–180	180–240	240–300	300–900	900–1500
Current peak value (A)	50	100	150	200	250	181.5	0

Table 2 Pressure vs. time during SPS process.

Time (sec)	0–60	60–120	120–180	180–240	240–300	300–900	900–1500
Pressure (kN)	1.5	1.7	1.9	1.7	1.2	4.5	0

on the details of the temperature distribution in electrode and CoSb₃-based thermoelectric materials during sintering process.

To the best of our knowledge, the temperature is generally tested by focusing a pyrometer or infrared thermometer on the outer die wall surface during SPS process, but it could not give the real temperature distribution in sample, the most effective way to find this out might be numerical simulation.⁴⁾ In the present study, we prepared Mo/Ti/CoSb₃ samples by SPS technique, and simulated the temperature distribution of sample during sintering with finite element method, observed the microstructures in CoSb₃ region using scanning electron microscope (SEM), and measured the thermal conductivity in CoSb₃ region by laser flash method. Furthermore, we discussed how to optimize the properties of CoSb₃-based compound from the point of view of the thermal conductivity and the electrical resistivity, respectively.

2. Experimental Procedure

One-step sintering experiments of Mo/Ti/CoSb₃ materials were carried out using SPS apparatus (SPS-2040, Sumitomo Coal Mining Co., Tokyo, Japan), and the schematic of the SPS apparatus was showed in Fig. 1. In order to produce a present time-temperature profile during sintering, power is controlled through the application of voltage difference on the ends of top and bottom electrode plates, and the pulse current flows into top electrode plate, through upper spacer plate, upper punch, graphite die (Shanghai Toyo Tanso Company Limited, Japan) set that contains the sample, lower punch, and then flows out from bottom electrode plate of the apparatus. Meanwhile, the thermocouple is located in half-way point between the interior and exterior wall of the graphite die where was drilled hole for temperature monitoring.

During SPS process, using a pulse current of 12 ms on and 2 ms off, and the pulsed current value at different sintering stages were given in Table 1. Mo/Ti/CoSb₃ materials were loaded into the graphite die of 10 mm inner diameter and punch unit, the uniaxial pressure applied on the upper spacer plate were kept constant at each minutes, and the pressure at different sintering stages were showed in Table 2. Heat was generated while electrical current flowing through all components of SPS apparatus, the temperature showed in the thermocouple increased from 35.6°C to 590°C in 5 mins, and the holding time was 10 mins at 590°C before turning off the power and removing the pressure. Finally, the disk shaped Mo/Ti/CoSb₃ multi-layer sample was simultaneously prepared by one-step SPS sintering process in a vacuum.

Fig. 1 Schematic of the SPS apparatus.

3. Theoretical Model

Joule heating occurs when a pulse DC flowing through the sintering system and the heat generation causes temperature change of the material. Owing to the thermal property and the electrical property of the material being dependent on temperature, the variable material properties would influence the thermal and electrical transfer during the sintering process. Therefore, the theoretical model is transient and thermal-electrical coupling, and the governing equations based on Ohm's and Fourier's laws for electrical and thermal analyses can be written as following eqs. (1) and (2), respectively

$$\nabla^2 \phi / \rho_e = 0 \quad (1)$$

Where ϕ is voltage, ρ_e is electrical resistivity.

$$\rho C_p \frac{\partial T}{\partial t} - k \nabla^2 T = \dot{q} \quad (2)$$

Where ρ , C_p , T , k and $\dot{q}$ represent density, specific heat, temperature, heat conductivity and amount of heat generation per second, $\dot{q} = |\nabla \phi|^2 / \rho_e$.

Boundary and initial conditions are established for the governing equations, and the boundary conditions for the electrostatic potential are as follows

$$\phi = \phi_0 \text{ at the top electrode} \quad (3a)$$

$$\phi = 0 \text{ at the bottom electrode} \quad (3b)$$

$$\partial\phi/\partial r = 0 \text{ at the outer surface of the die} \quad (3c)$$

The SPS process takes place in vacuum, so heat loses mainly by radiation from all the lateral surfaces towards surrounding environment, especially at high temperature; and there is heat loss by convection towards water cooled electrodes.

The heat transfer by radiation can be determined by Stefan-Boltzmann law

$$\dot{q}_r = \sigma_s * \varepsilon * (T_e^4 - T_s^4) \quad (4a)$$

with $\dot{q}_r$, the heat loss per unit time per unit surface, σ_s , Stefan-Boltzmann constant, ε , the emissivity, T_e , the temperature of emitting surface, T_s , the temperature of surrounding environment.

In the present case, the heat transfer was modeled as a convective heat transfer due to the contact of the spacer plates with the water cooled electrodes. Convection can be described by

$$\dot{q}_c = h * (T_p - T_w) \quad (4b)$$

with T_p , T_w and h are the temperature of the spacer plates near the contact surfaces, the temperature of the cooling water and the convection coefficient, respectively.^{1,6,11,12)}

4. Finite Element Simulation

In view of the symmetry, two-dimensional modeling was adopted in the simulation, and thermal-electrical coupling elements were employed due to the relatively high dependence of thermal and electrical properties on the temperature. Because thermal conductivity and electrical conductivity of the powder could not be measured exactly at present, the thermal conductivity and electrical conductivity of CoSb₃ and Ti in solid state were used. But the variation of thermal conductivity and electrical conductivity with temperature during sintering was considered and the effect of thermal conductivity and electrical conductivity on temperature distribution in sample was discussed in details, so although the densification process was not treated like it was, yet could be reflected at a certain extent. The graphite was also treated as isotropic in the model due to the measured properties of graphite using as die, punches and spacer plates being quite uniform. Despite this simplification, the results serve to shed light on the important consequences of temperature distributions in the SPS process.⁶⁾ A schematic of the spark plasma sintering apparatus used in the experiments and simulation was shown in Table 3.

The reliable material property parameters dependent on temperature in the simulation were measured. The electrical resistivity of CoSb₃, Ti, Mo and graphite was measured by standard DC four-probe method in a flowing Ar atmosphere. The thermal conductivity of CoSb₃, Ti, Mo and graphite were measured by laser flash method (Netzsch, LFA427). The density of material at several temperatures was calculated using the thermal expansion coefficient measured by Netzsch DIL 402C. The specific heat of CoSb₃ and graphite was measured by ASTM E1269-05 (PE DSC-2C), and the specific

Table 3 The scale specifications of SPS Components and material in Fig. 1.

Scale of SPS components and material	Outer diameter/inner diameter/thickness
CoSb ₃	Outer diameter: 10 mm; thickness: 8 mm
Ti	Outer diameter: 10 mm; thickness: 200 μ m
Mo	Outer diameter: 10 mm; thickness: 1.2 mm
Upper/Lower punch (graphite)	Outer diameter: 10 mm; thickness: 20 mm
Die (graphite)	Outer diameter: 30 mm; inner diameter: 10 mm thickness: 30 mm
Spacer plate (graphite)	Outer diameter: 120 mm; thickness: 40 mm

heat of Mo and Ti only slightly depends on temperature, therefore a constant value was used during simulation. Thermal conductivity, electrical resistivity, specific heat and density applied in the simulation were listed in appendix.

The contact interface existed between the spacer plates, the punch and the spacer plate, and two thin graphite papers were placed on the top and bottom surface of the sample respectively to prevent possible contamination to the punches, similarly, one graphite paper was set between the sample and the die, thus the thermal and electrical properties are discontinuous at the interface, and the contact electrical resistance and thermal resistance between all contact interface should be taken into account.^{1,4)} By measuring the electrical resistance of the two-layer graphite papers and the electrical resistance of the sample, respectively, and the total electrical resistance of two-layer graphite papers and sample under the same pressure as the experiments, the contact resistance between graphite paper and sample was obtained, and the contact resistance between punch and graphite paper could be know by the same way, so the resistance of two graphite papers and corresponding contact interface could be obtained and used as resistance of the horizontal graphite papers in simulation for simplification. The electrical resistivity of the horizontal graphite papers was determined by the relationship of resistance and resistivity, and supposed the variation of electrical resistivity with temperature is same as graphite. The thermal conductivity of horizontal graphite papers in simulation could be calculated as the method of literature 1), and it was assumed to be inversely proportional to the electrical resistivity, $\lambda_p = \eta \lambda_{gr} \rho_{gr} / \rho_p$, where λ and ρ are the thermal conductivity and electrical resistivity respectively, p and gr denote the horizontal graphite papers and graphite, η is a fitting coefficient and was supposed to be 1.2. The electrical resistivity and thermal conductivity of vertical graphite papers used as simulation were acquired by similar manner. The specific heat and density of the graphite papers were taken to be same as that of the graphite. The electrical resistivity between the spacer plates, the punch and the spacer plate were derived from matching experiments with simulations, corresponding thermal conductivity could be calculated as the above method, and specific heat and density were taken to be similar to that of graphite. Fan *et al.*¹⁰⁾ indicated that the intermediate layers formed around the interface of Mo/Ti/CoSb₃ sample did not bring any electrically resistive layers. The interfacial resistance in the present sample was

minimized, thus the contact resistance in the interface between CoSb₃ and Ti, Ti and Mo were ignored. All the contact electrical resistivity and thermal conductivity were also given in the appendix. Although the contact electrical resistivity and thermal conductivity could not quite accurately reflect the physical circumstances, it can shed considerable light on the material parameters at the contact zone during the simulation process of temperature.

In the simulation, the initial temperature of the whole system was set to be 35.6°C, the boundary temperature at the top, bottom water-cooled electrodes and surrounding environment were kept at a constant temperature of 35.6°C according to the actual temperature in experiments. Uniform pressures showed in Table 2 were applied on the top boundary, and zero vertical displacements were assumed for the bottom boundary. Although these boundary conditions do not exactly reflect the actual experimental conditions, they are considered appropriate approximations. The emissivity of graphite only slightly depends on temperature and was taken to be 0.8, and the convection coefficient was 880 W/(m.K), in agreement with literature data.¹⁾

5. Results and Discussion

The temperature distributions of Mo/Ti/CoSb₃ sample during spark plasma sintering were simulated using the theoretical model and experimental data mentioned above.

Figure 2 shows the measured and simulated temperatures at the halfway point of graphite die wall during sintering and holding stages. The simulated temperatures are slightly lower than the measured temperatures in the front two minutes of sintering, after that, the simulated and measured temperatures agreed very well. The reason for this phenomenon could be that the parameters of CoSb₃ and Ti bulk material instead of that of powder were used in simulation. Actually, in the early stage of sintering, powder particles were packed loosely, little contact surface between particles led to high electrical resistivity, and then more heat was generated during this stage. Subsequently the pulse current caused a spark discharge between particles of the powder and induced the formation of the necks by volume diffusion through the contact points of adjacent powder particles,³⁾ with the partial

Fig. 2 The measured and simulated temperatures in the center of graphite die wall during sintering and holding time.

Fig. 3 Temperature in the spacer plates/punches/sample/die system at sintering 120 seconds T/°C.

Fig. 4 Temperature distribution in Mo/Ti/CoSb₃ sample at sintering 120 seconds (a) and 240 seconds (b) T/°C.

contact surfaces vanishing, the electrical resistivity of CoSb₃ and Ti gradually decreased and closed to that of bulk material, the measured temperatures fit well with the simulated temperatures. It could be inferred that the simulated temperatures may mirror true temperatures during the later stages of sintering.

Figure 3 shows the temperature distribution in the spacer plates/punches/sample/die system at sintering 120 seconds, the highest temperature region in the system concentrated on the punches and the sample due to high current density in punches, and high electrical resistivity in the sample, particularly the influence of the contact resistance around the sample. From above analysis, it is known that the measured temperature by thermocouple set in die wall is lower than that of sample. Thus, the measured temperature could not reflect actual temperature in the sample. Therefore, it is confirmed again that it is necessary to simulate the temperature distribution of the sample during SPS process.

Generally, we more concern about the temperature in the sample during sintering. Figure 4 illustrates the temperature distribution at sintering 120 and 240 seconds, respectively. As displayed in Fig. 4, the temperature and temperature gradient increased with increasing sintering time, the highest temperature in sample from 168.28°C at 120 seconds

Fig. 5 Variation of temperature distribution in Mo/Ti/CoSb₃ sample with thermal conductivity of CoSb₃-based compound at holding 600 seconds (a) 0.5*k* (b) 0.75*k* (c) *k*, T/°C.

increased to 485.71°C at 240 seconds, and the temperature gradient increased from 7.05°C at 120 seconds to 33.98°C at 240 seconds. It is also noted that the temperature in central region of the sample was higher than that of the borders due to heat loss by radiation from the border surfaces of sintering system. The radial temperature gradient in CoSb₃ was higher than that of Mo and Ti, and the reason may be that the lower thermal conductivity of CoSb₃ led to slower thermal diffusion. The highest temperature in the Mo/Ti/CoSb₃ sample was existed in CoSb₃ region, which could be explained that more heat was produced in CoSb₃ region while current flowing through the sample attributing to the greater electrical resistivity of CoSb₃.

Although binary CoSb₃ exhibits good electrical transport properties, but the ZT value is not very high for the relatively high thermal conductivity. In order to enhance the thermoelectric property, doping and/or filling are performed.^{13–18)} By inserting filler atom such as rare-earth or alkaline earth atom into Sb-icosahedron voids of the binary CoSb₃, the lattice thermal conductivity was reduced greatly due to rattling of filler atoms around their equilibrium positions, and efficiently scattering the phonons. The filler atoms also significantly affect electrical transport properties such as carrier concentration and mobility by Wiedemann-Franz law. On the other hand, doping was also reported to reduce lattice thermal conductivity as well as control carrier concentration considerably. The substitution for Co or Sb by dopants can influence the electronic structure, increase carrier concentration and electric conductivity of the material. Furthermore, the increase of content of dopant can be very effective in reducing lattice thermal conductivity due to enhanced scattering of phonons on impurities. And hot junction of TE devices studied serves at moderate temperature in long-term state, thus it is necessary to study the effect of the thermal conductivity and the electrical resistivity of CoSb₃-based compound on temperature gradient in the sample during holding time.

Figure 5 depicts temperature gradient variation in Mo/Ti/CoSb₃ sample with thermal conductivity of CoSb₃-based compound at the final stage of holding time, where *k*, the thermal conductivity of pure CoSb₃ being dependent on

temperature, listing in Table A-1 of appendix. The temperature gradient in sample acquired from calculation was 22.38°C shown in Fig. 5(a), 16.29°C shown in Fig. 5(b) and 12.94°C shown in Fig. 5(c), respectively, and it could be concluded that the lower the thermal conductivity of CoSb₃-based compound, the greater the temperature gradient in sample. Actually, owing to the thermal conductivity of CoSb₃ in solid state used in the simulation instead of that of powders, the true temperature gradient in CoSb₃ region should slightly higher than the above results. For thermoelectric material, the heat is carried mainly by phonons, charge carriers and photons, otherwise the TE devices are usually used at low and moderate temperature, and thus the contribution of photons might be ignored.¹⁹⁾ In order to enhance the thermoelectric property, by doping and/or filling, the thermal conductivity of TE material could be reduced due to the coupling effect of electron-phonon scattering.¹⁴⁾ As a result, slower thermal diffusion may induce greater temperature gradient in sample.

Figure 6 depicts the temperature gradient variation in Mo/Ti/CoSb₃ sample with electrical resistivity of CoSb₃-based compound at the final stage of holding time, where ρ_e , the electrical resistivity of pure CoSb₃ being dependent on temperature, listing in Table A-2 of appendix. The temperature gradient in sample acquired from calculation was 9.13°C shown in Fig. 6(a), 11.42°C shown in Fig. 6(b) and 12.94°C shown in Fig. 6(c), respectively. It could be concluded that the lower the electrical resistivity of CoSb₃-based compound, the smaller the temperature gradient in sample. In the microscopic theory, the electrical resistivity is determined by the contribution of each of charge carrier with its concentration, effective mass and relaxation time. The electrical resistivity decreases while carrier concentration increase, and the impact of the effective mass and relaxation time on the electrical resistivity is generally weak under the conditions of no temperature change and strong external influence.¹⁹⁾ Hence by doping and/or filling, the carrier concentration increases and the electrical resistivity decreases, further by Wiedemann-Franz law, the thermal conductivity increases, and using the above analysis about Fig. 5, the temperature gradient in sample decreases.

Fig. 6 Variation of temperature distribution in Mo/Ti/CoSb₃ sample with electrical resistivity of CoSb₃-based compound at holding 600 seconds (a) $0.5\rho_e$ (b) $0.75\rho_e$ (c) $\rho_e T/^{\circ}\text{C}$.

Fig. 7 Scanning electron microscope images of surface topography in CoSb₃ region of sample (a) the position of A region and B region in sample (b) A region image (c) B region image.

The dependence of temperature in the sample on the microstructure of CoSb₃ was investigated by SEM. The surface micrographs of different temperature regions in CoSb₃ were shown in Fig. 7, and it can be seen that the average grain size in A region is slightly smaller than that of B region, which could be explained by grain growth kinetics theory that the higher the temperature, the faster the growth speed of grain. Furthermore, the mechanical property may be influenced by the non-uniform microstructure, based on hall-petch formula, the smaller the grain size, the better the strength, so fine grain size could enhance the strength of material, as mentioned in literature [20]. Additionally the thermal conductivity of A region and B region in CoSb₃ was measured by laser flash method (Netzsch, LFA427) and shown in Fig. 8, and the effect of microstructure on thermal conductivity of CoSb₃ was analysed, the results indicated that the thermal conductivity of CoSb₃ descends with decreasing average grain size. The reason may be intensified scattering of grains boundary to phonons reduced the lattice thermal conductivity greatly, the thermal conductivity was decreased and thermoelectric property may be enhanced. From above analysis, the temperature gradient in sample during sintering would influence mechanical property and thermoelectric property of CoSb₃ material, so it should be decreased to the best of our abilities.

Fig. 8 Thermal conductivity of A region and B region in CoSb₃ of the sample.

Determining how to optimize the properties of CoSb₃-based compound is important for the Mo/Ti/CoSb₃ materials used as TE couples. From the point of view of thermal conductivity, the mechanical property and thermoelectric property are two competing factors. The mechanical property could be non-uniform due to non-uniform microstructure induced by greater temperature gradient with a decrease in thermal conductivity. On the other hand, the thermoelectric

property could be enhanced with decreasing thermal conductivity. Therefore, the thermal conductivity should be optimized appropriately by rational choice of dopant and/or filler atom and precise determination of doping and/or filling quantity to meet the requirement of material property used as TE devices. From the point of view of electrical resistivity, the mechanical property could be uniform due to relatively uniform microstructure induced by smaller temperature gradient with decreasing electrical resistivity. In addition, the lower electrical resistivity could improve thermoelectric property of CoSb₃-based compound. Therefore, the low electrical resistivity is beneficial to the improvement of both the mechanical and thermoelectric properties for material used as TE devices at a certain extent.

6. Conclusions

The temperature distribution and evolution of Mo/Ti/CoSb₃ materials used as thermoelectric couple of TE device were simulated by finite element method, the microstructures in different temperature regions of CoSb₃ were observed by SEM, and the thermal conductivity in different temperature regions of CoSb₃ were measured by laser flash method. In the end, the optimization of CoSb₃-based compound properties was discussed in details. The main points of the present study are as follows:

(1) The simulation agree well with the available experimental data, such as the die interior temperature measured by thermocouple during sintering process. The sample and punches have the higher temperature in the whole sintering process, in which the highest temperature existed in CoSb₃ region, and the radial temperature gradient of CoSb₃ is obvious.

(2) The temperature gradient in sample results in non-uniform microstructure and thermal conductivity difference, which may further influence the mechanical property and thermoelectric property of CoSb₃, so the temperature gradient in sintering should be decreased to the best of our abilities, for example, the graphite die is surrounded by insulation carbon felt to minimize heat losses and reduce temperature gradient.

(3) The temperature gradient increases with decreasing thermal conductivity and increasing electrical resistivity of CoSb₃-based compound. And the thermal conductivity of CoSb₃-based compound should be rationally optimized and the electrical resistivity of CoSb₃-based compound should be decreased at a certain extent to improve simultaneously the mechanical property and thermoelectric property of CoSb₃ material used as TE device.

In this study, the qualitative analysis about the effect of temperature gradient on the combined thermoelectric property and mechanical property of material used as TE devices was done, and the quantitative study about the effect of temperature gradient on material strength, seebeck coefficient, and etc. is required in the future research work.

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REFERENCES

- 1) K. Vanmeensel, A. Laptev, J. Hennicke, J. Vleugels and O. Van der Biest: *Acta Mater.* **53** (2005) 4379–4388.
- 2) K. A. Khor, L. G. Yu, O. Andersen and G. Stephani: *Mater. Sci. Eng. A* **356** (2003) 130–135.
- 3) E. Fleury, J. H. Lee, S. H. Kim, W. T. Kim, J. S. Kim and D. H. Kim: *Metall. Mater. Trans. A* **34** (2003) 841–849.
- 4) A. Zavaliangos, J. Zhang, M. Krammer and J. R. Groza: *Mater. Sci. Eng. A* **379** (2004) 218–228.
- 5) W. Yucheng and F. Zhengyi: *Mater. Sci. Eng. B* **90** (2002) 34–37.
- 6) X. Wang, S. R. Casolco, G. Xu and J. E. Garay: *Acta Mater.* **55** (2007) 3611–3622.
- 7) U. Anselmi-Tamburini, S. Gennari, J. E. Garay and Z. A. Munir: *Mater. Sci. Eng. A* **394** (2005) 139–148.
- 8) F. J. DiSalvo: *Science* **285** (1999) 703–706.
- 9) S. Furuyama, T. Iida, S. Matsui, M. Akasaka, K. Nishio and Y. Takanashi: *J. Alloy. Compd.* **415** (2006) 251–256.
- 10) J. Fan, L. Chen, S. Bai and X. Shi: *Mater. Lett.* **58** (2004) 3876–3878.
- 11) E. M. Heian, A. Feng and Z. A. Munir: *Acta Mater.* **50** (2002) 3331–3346.
- 12) K. Matsugi, H. Kuramoto, T. Hatayama and O. Yanagisawa: *J. Mater. Process. Technol.* **146** (2004) 274–281.
- 13) X. Y. Zhao, X. Shi, L. D. Chen, W. Q. Zhang, W. B. Zhang and Y. Z. Pei: *J. Appl. Phys.* **99** (2006) 053711.
- 14) L. Yang, J. S. Wu and L. T. Zhang: *J. Alloy. Compd.* **375** (2004) 114–119.
- 15) A. Weidenkaff, R. Robert, M. Aguirre, L. Bocher, T. Lippert and S. Canulescu: *Renewable Energy* **33** (2008) 342–347.
- 16) G. Chen, M. S. Dresselhaus, G. Dresselhaus, J.-P. Fleurial and T. Caillat: *Int. Mater. Rev.* **48** (2003) 45–66.
- 17) K. T. Wojciechowski: *Mater. Res. Bull.* **37** (2002) 2023–2033.
- 18) S.-Chul Ur, J.-Chul Kwon and Il-Ho Kim: *J. Alloy. Compd.* **442** (2007) 358–361.
- 19) L. I. Anatychuk: *Physics of thermoelectricity*, (Institute of Thermoelectricity Kyiv, Chernivtsi, 1998) pp. 172–177.
- 20) A. L. Chamberlain, W. G. Fahrenholtz, G. E. Hilmas and D. T. Ellerby: *J. Am. Ceram. Soc.* **87** (2004) 1170–1172.

Appendix

Table A-1 Variation of thermal conductivity with temperature.

Material	Thermal conductivity (W/(m·°C)) (30°C–590°C)
Mo	$k = 149.25334 - 0.10275T + 0.00111T^2 - 6.78401 * 10^{-6}T^3 + 1.9908 * 10^{-8}T^4 - 2.75193 * 10^{-11}T^5 + 1.43721 * 10^{-14}T^6$
Ti	$k = 25.18267 - 0.05532T + 6.29929 * 10^{-4}T^2 - 3.6199 * 10^{-6}T^3 + 9.94248 * 10^{-9}T^4 - 1.30889 * 10^{-11}T^5 + 6.62448 * 10^{-15}T^6$
CoSb ₃	$k = 9.79194 - 0.01509T - 5.55976 * 10^{-5}T^2 + 4.4111 * 10^{-7}T^3 - 1.40501 * 10^{-9}T^4 + 2.41494 * 10^{-12}T^5 - 1.61659 * 10^{-15}T^6$
Graphite	$k = 147.93865 - 0.98518T + 0.01158T^2 - 8.10465 * 10^{-5}T^3 + 2.84086 * 10^{-7}T^4 - 4.76517 * 10^{-10}T^5 + 3.06812 * 10^{-13}T^6$
Contact zone between sample and punch	$k = 3.79772 - 0.03166T + 3.9865 * 10^{-4}T^2 - 2.71641 * 10^{-6}T^3 + 9.29354 * 10^{-9}T^4 - 1.52603 * 10^{-11}T^5 + 9.62929 * 10^{-15}T^6$
Contact zone between sample and die	$k = 0.53943 - 0.00438T + 5.51988 * 10^{-5}T^2 - 3.79183 * 10^{-7}T^3 + 1.30768 * 10^{-9}T^4 - 2.16278 * 10^{-12}T^5 + 1.3739 * 10^{-15}T^6$
Contact zone between spacer plates, punch and spacer plate	$k = 5.59574 - 0.05381T + 6.98039 * 10^{-4}T^2 - 4.64707 * 10^{-6}T^3 + 1.55288 * 10^{-8}T^4 - 2.48408 * 10^{-11}T^5 + 1.52304 * 10^{-14}T^6$

Table A-2 Variation of electrical resistivity with temperature.

Material	Electrical resistivity (μΩ·m) (30°C–590°C)
Mo	$\rho_e = 0.04354 + 3.72785 * 10^{-4}T - 3.72248 * 10^{-6}T^2 + 2.61965 * 10^{-8}T^3 - 8.40753 * 10^{-11}T^4 + 1.30402 * 10^{-13}T^5 - 7.85607 * 10^{-17}T^6$
Ti	$\rho_e = 0.42049 - 1.03985 * 10^{-4}T + 3.994 * 10^{-6}T^2 - 2.48363 * 10^{-8}T^3 + 7.41836 * 10^{-11}T^4 - 1.05939 * 10^{-13}T^5 + 6.04113 * 10^{-17}T^6$
CoSb ₃	$\rho_e = 614.16726 - 1.02441T - 0.01305T^2 + 3.48145 * 10^{-6}T^3 + 2.79458 * 10^{-7}T^4 - 7.80748 * 10^{-10}T^5 + 6.19791 * 10^{-13}T^6$
Graphite	$\rho_e = 18.68446 - 0.02809T + 1.04582 * 10^{-5}T^2 + 2.7188 * 10^{-7}T^3 - 1.10134 * 10^{-9}T^4 + 1.77644 * 10^{-12}T^5 - 1.04318 * 10^{-15}T^6$
Contact zone between sample and punch	$\rho_e = 952.90999 - 3.45164T + 0.02852T^2 - 1.64632 * 10^{-4}T^3 + 4.83117 * 10^{-7}T^4 - 6.8372 * 10^{-10}T^5 + 3.69562 * 10^{-13}T^6$
Contact zone between sample and die	$\rho_e = 6670.36994 - 24.16147T + 0.19963T^2 - 0.00115T^3 + 3.38182 * 10^{-6}T^4 - 4.78604 * 10^{-9}T^5 + 2.58693 * 10^{-12}T^6$
Contact zone between spacer plates, punch and spacer plate	$\rho_e = 682.3227 - 3.10079T + 0.02876T^2 - 1.74083 * 10^{-4}T^3 + 5.20556 * 10^{-7}T^4 - 7.44639 * 10^{-10}T^5 + 4.06619 * 10^{-13}T^6$

Table A-3 Variation of specific heat with temperature.

Material	Specific heat (J/(kg·K)) (30°C–590°C)
Mo	$C_p = 258$
Ti	$C_p = 540$
CoSb ₃	$C_p = 215.06147 + 0.05089T - 4.84899 * 10^{-5}T^2 - 2.80711 * 10^{-8}T^3 + 9.93582 * 10^{-11}T^4 - 1.63194 * 10^{-13}T^5 + 1.00218 * 10^{-16}T^6$
Graphite	$C_p = 741.99409 + 2.09018T + 0.00858T^2 - 9.63946 * 10^{-5}T^3 + 4.18839 * 10^{-7}T^4 - 8.50981 * 10^{-10}T^5 + 6.54463 * 10^{-13}T^6$

Table A-4 Variation of density with temperature.

Material	Density (Kg/m ³) (30°C–590°C)
Mo	$\rho = 10208.16124 - 0.28074T + 9.24716 * 10^{-4}T^2 - 2.81293 * 10^{-6}T^3 + 2.53985 * 10^{-9}T^4$
Ti	$\rho = 4503.18171 - 0.09887T - 2.43076 * 10^{-4}T^2 + 1.20319 * 10^{-6}T^3 - 1.59991 * 10^{-9}T^4$
CoSb ₃	$\rho = 7595.67232 - 0.18426T - 3.21289 * 10^{-4}T^2 + 5.18784 * 10^{-7}T^3 - 2.01892 * 10^{-10}T^4$
Graphite	$\rho = 1781.23725 - 0.04846T + 2.90921 * 10^{-4}T^2 - 1.95178 * 10^{-6}T^3$ $+ 6.21812 * 10^{-9}T^4 - 9.58283 * 10^{-12}T^5 + 5.73301 * 10^{-15}T^6$