Transient response of thermoelectric elements and dynamic measurement methods for thermoelectric materials

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Content

1. Fundamental equations for transient response
   Continuum theory – thermoelectricity

2. Direct and inverse problems

3. Transient performance calculations

4. Dynamic measurements (thermal conductivity)
   - Combined thermoelectric measurement (CTEM)
Thermoelectricity – Continuum approach

- Continuum theory: Description of the properties and measurements of thermoelectrics on a macroscopic level

- Characteristic time and length scales $\tau \geq 10^{-3}$ s and $l \geq 10^{-3}$ m

- Transport of energy and charges – description via differential equations, thermal energy balance equation

$$\vec{E}[\vec{r}(t), t] \quad T[\vec{r}(t), t]$$

Electric field \hspace{1cm} Temperature field

Continuum theory: Two main categories of equations

Equations independent of the material: kinematic relations of the continuum, loading parameters, balance equations

Equations dependent on the material: Coverage and description of material properties

Conservation laws

Constitutive equations
Thermoelectricity – Generalized heat equation

Conservation equations

Differential form

- Charge conservation
  \[ \nabla \cdot \vec{j} = 0 \]

- (thermal) energy conservation
  \[ \varrho_d \ c \ \frac{\partial T}{\partial t} + \nabla \cdot \vec{J}_Q = \vec{j} \cdot \vec{E} \]

Constitutive equations

Onsager’s linear response theory

- Generalized Fourier’s law – Heat flux
  \[ \vec{J}_Q = -\kappa \nabla T + \alpha T \vec{j} = \vec{J}_{Q,\kappa} + \vec{J}_{Q,\pi} \]

- Generalized Ohm’s law – Electrical current density
  \[ \vec{j} = \sigma \vec{E} - \sigma \alpha \nabla T \]

\[ \varrho_d \ c \ \frac{\partial T}{\partial t} - \nabla \cdot (\kappa \nabla T) + \tau \vec{j} \cdot \nabla T = \frac{j^2}{\sigma} \]

\( \tau = T \frac{\partial \alpha}{\partial T} \) ... Thomson coefficient, \( \varrho_d \) ... mass density, \( c \) ... specific heat capacity, \( \kappa \) ... thermal conductivity,
\( \alpha \) ... Seebeck coefficient, \( \sigma \) ... electrical conductivity

Solution of heat equation in thermoelectricity

Direct problem
Initial values, boundary conditions, material properties
well-posed problem

Inverse problem
Not all values are given, Experimental data for estimation of boundary values
ill-posed problem

- Initial conditions (IC)
  Temperature distribution at \( t = 0 \): \( T_0[\vec{r}(t)] \)

- Boundary conditions (BC)
  - Dirichlet/Neumann/mixed BC
  [Boundary value problem (BVP)]

\[ Q_d c \frac{\partial T}{\partial t} - \nabla \cdot (\kappa \nabla T) + \tau \vec{j} \cdot \nabla T = \frac{j^2}{\sigma} \]

Performance calculation of thermoelectric devices and systems

Determination of parameters in measurements systems, e.g. material properties
Performance calculation of thermoelectric devices

**Thermoelectric Generator (TEG)**
- Heat Source
- Cool Side
- Variation of $R_L$ or $I$
- Electrical power output $P_{el}$
- Efficiency $\eta$
- Heat flow $\dot{Q}$
- Coefficient of performance $\phi$

**Direct solution of the heat equation**
- Material properties
- Fixed boundary temperatures
- Fixed heat input

**Thermoelectric Cooler (TEC)**
- Cooled Surface
- Dissipated Heat
- Variation of $R_L$ or $I$

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**Equation:**
$$T(\vec{r}, t)$$

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www.DLR.de • Chart 6
Transient response in thermoelectricity

- Time dependent fields $T = T(\vec{r}, t)$ and $\vec{E} = \vec{E}(\vec{r}, t)$

- Dynamic working conditions:

  - BC: $T_h = T_h(t)$, $T_c = T_c(t)$, $\dot{Q}_h = \dot{Q}_h(t)$
  - Ambient: $T_{amb} = T_{amb}(t)$
  - Material: $\kappa = \kappa[T(\vec{r}, t), \vec{r}, t]$ e.g.
  - Load/Current: $R_L = R_L(t)$ or $I = I(t)$

- Solution of the generalized heat equation:
  - Steady state $\Rightarrow$ Ordinary differential equations
  - Transient response $\Rightarrow$ Partial differential equations

- Analytical solutions only in particular cases with help of integral transformation (e.g. Laplace) or in a (Fourier) series expansion

- Approximative or numerical solution methods (CPM, FEM, FDM, Circuits...)

Transient performance calculations

- Quasi-stationary processes ⇒ Timescale of changes in the working/boundary conditions much greater than response time of the thermoelectric system ⇒ use of steady state equations for different times

- TEC pulsed supercooling


- Transient TEG


Montecucco et al., Appl. Therm. Eng. 35 (2012) 177-184
Nguyen/Pochiraju, Appl. Therm. Eng. 51 (2013) 1-9
Meng, J. Power Sources, 245 (2014) 262-269

- AC impedance spectroscopy

García-Cañadas/Min (previous talk), J. Electr. Mat. 43, 2411 (2014)
C. Goupil (talk yesterday), J. Stockholm (poster yesterday)

Thermal conductivity for semiconductors often small ⇒ ≈1 W/(m K)
- Small samples, mechanically not easy to be processed
- Brittleness ⇒ not possible to put in thermocouples in the sample
- Hard to realize a good thermal contact via soldering
- Specific heat often not known

Measurement techniques \( \kappa \)

- Steady-state/stationary methods
  - Absolute technique
  - Comparative technique

- Dynamic/transient methods
  - Laser Flash Thermal Diffusivity Method
  - Generalized Ioffe method ⇒ CTEM
  - 3\( \omega \) method
  - time-domain thermoreflectance

Inverse heat conduction problems

- Inverse heat conduction problems (IHCP)

Temperatures $T$ measured (at some points, times)

- Classification IHCP:
  - Material properties determination inverse problems,
  - Boundary value determination inverse problems,
  - Initial value determination inverse problems,
  - Source determination inverse problems,
  - Shape determination inverse problems

- Unknown thermal conductivity (material property) ⇒ inverse calculation

- Solution of the direct problem to get insights how to solve the IHCP

CTEM – Measurement of thermal conductivity

- Combined thermoelectric measurement (CTEM):

- Simultaneous measurement method ⇒ all TE properties including Harman-$ZT$
- Here: focus on thermal conductivity measurement

- Generalized Ioffe method

    Decrease of $\Delta T$

    Thermal conductivity $\kappa$

More experimental details on Poster P3.30
H.Kolb today
Transient temperature difference

- Heating of one Cu block
- Switching off after reaching $\Delta T \approx 5K$
- Observing relaxation of temperatures

Relaxation time $\tau$

Thermal conductivity $\kappa_S$

$$\kappa_S = \frac{L_S}{2A_{c,s}} \frac{m_b c_b}{\tau} \left(1 + \frac{m_S c_S}{6 m_b c_b} \right)$$
Solution of the direct problem – Simple Ioffe method

- Simple Ioffe method (sample and one block):
  1. Analytical solution as Fourier series
  2. Numerical solution with ANSYS (FEM)

System of PDE

\[
\begin{align*}
\frac{\partial T_1}{\partial t} &= \alpha_{d,1} \frac{\partial^2 T_1}{\partial x^2} \\
\frac{\partial T_2}{\partial t} &= \alpha_{d,2} \frac{\partial^2 T_2}{\partial x^2}
\end{align*}
\]

BC

\[ T_1(x = 0, t) = T_{\text{amb}} \]

IC

\[ T_1(x, t = 0) = T_{\text{amb}} \quad \quad T_2(x, t = 0) = T_0 > T_{\text{amb}} \]

Interface

\[ T_1(x = L_1-, t) = T_2(x = L_1+, t) \quad -\kappa_1 \left( \frac{\partial T_1}{\partial x} \right)_{x=L_1-} = -\kappa_2 \left( \frac{\partial T_2}{\partial x} \right)_{x=L_1+} \]
Sequences of transient simulations

- Short time behavior – heat wave through the sample – non-exponential

\[ t = 10^{-4} \text{ s} \quad t = 10^{-1} \text{ s} \quad t = 1 \text{ s} \]

Temperature

Heat flux
Relaxation of temperature difference

- Relaxation to equilibrium exponential

\[ \tau = (M_1)^{-1} \quad \text{... relaxation time (from the experiment)} \]

\[ C_1 = m_1 c_1 = \varepsilon_{d,1} V_1 \quad \text{... thermal mass of the sample} \]

\[ C_2 = m_2 c_2 = \varepsilon_{d,2} V_2 \quad \text{... thermal mass of the block} \]

\[ \kappa_1 = \frac{L_1}{A_{c,s}} M_1 C_2 \left( 1 + \frac{\kappa_1 L_2}{3 \kappa_2 L_1} + \frac{C_1}{3 C_2} \right) \]

- Thermal conductivity after algebraic treatment and Taylor expansion (omitting terms of second order and higher)

- in the example calculation less than 1% approximation error
Influence factors on the relaxation time

- Contact resistance at the interface
  - $R^c_{th}$ [K/W]

- Radiation to the ambient
  - Emissivity $\varepsilon$
  - Ambient temperature $T_{amb}$
  - Significant at high $T$

- Fixed values of
  $$\tilde{\alpha}_c = \left( R^c_{th} A_{c,s} \right)^{-1} \quad [\text{W/m}^2 \text{K}]$$
- Symmetric for both side

- Errors
  - Underestimation of $\kappa$
  - Overestimation of $\kappa$

Zabrocki et al., J. Electr. Mat. 42 (7), 2402-2408 (2013)
CTEM – Peltier heat

- DC current through the assembly ⇒ Peltier heat at the contacts
- At which side of the contact is the Peltier heat liberated or absorbed?

3D Simulation

2D Simulation (axisymmetric)

- transient thermal simulation
- No holes for thermocouples
- Heat generation in a slice
- Contacts – bulk values of a slice

$\begin{align*}
    j \alpha_{bt} T & \quad j \alpha_s T & \quad j \alpha_{bt} T \\
    j (\alpha_{bt} - \alpha_s) T & \quad -j (\alpha_{bt} - \alpha_s) T
\end{align*}$
Contacts as a slide

- Three thin layers:
  - Metal block
  - Contact material
  - Sample

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Cu block  S  Cu block
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- Contacts through bulk values

- Heat generation in the metal block or sample?

- Galinstan (liquid metal solder)
  \[
  \kappa = 16.5 \ \text{W/m K} \\
  \rho_d = 6.44 \ \text{g/cm}^3 \\
  \sigma = 3.46 \cdot 10^6 \ \text{S/m} \\
  c_p = 200 \ \text{J/kg K}
  \]
Peltier heat from where?

- Peltier heat liberated or absorbed at the metal side or the sample side

![Graphs showing heat generation/absorption for metal and sample sides.](image-url)
Peltier heat – Qualify contact resistance

- Peltier-heat either liberated/absorbed at metal side or sample side of the contact material ⇒ different behavior at the switch-off

Metal

Sample

- Experimentally observed jump ⇒ Qualification of the thermal contact resistance
Summary

- Generalized heat equation in thermoelectricity for transient response

- Direct solution for the determination of the performance of TE devices

- Inverse problem: Determination of material properties from measurements of temperatures

- Dynamic measurement of the thermal conductivity – CTEM

Thank you for your attention!
The END