Audio test:

Termická analýza

02 Diferenciální termická analýza DTA

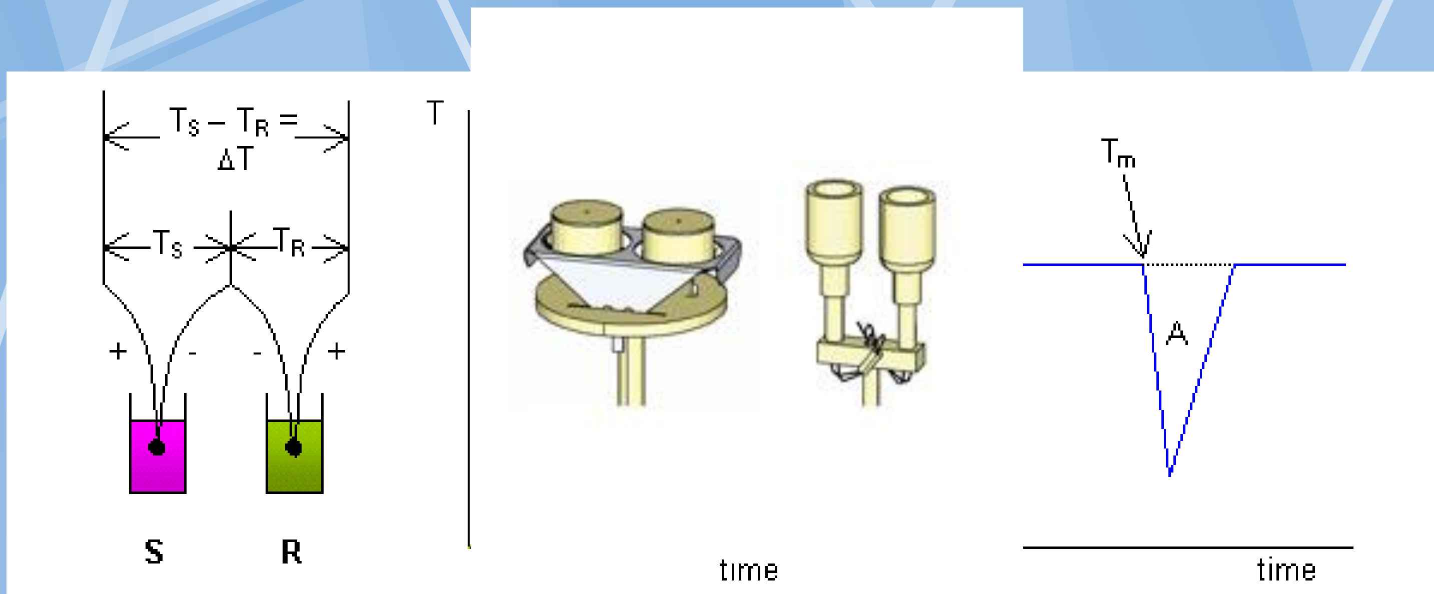
Přednášející: Doc. Jiří Sopoušek

Brno, prosinec 2011

Obsah

- Rozdíly DTA od DSC
- Citlivost a přesnost DTA vs. DSC
- Výhody DTA
- Použití

hfDSC vs. DTA



hfDSC DTA

Heat flow differential scanning calorimetry

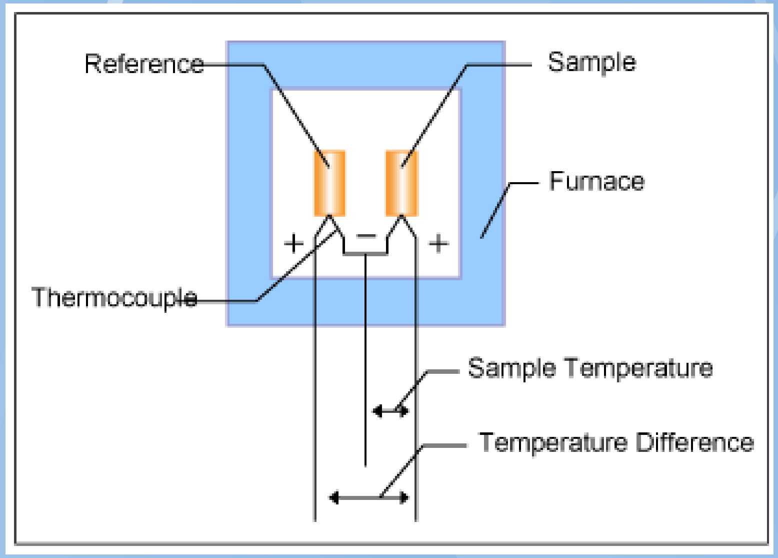
(Diderenciální skenovací kalorimetrie s tepelným tokem)

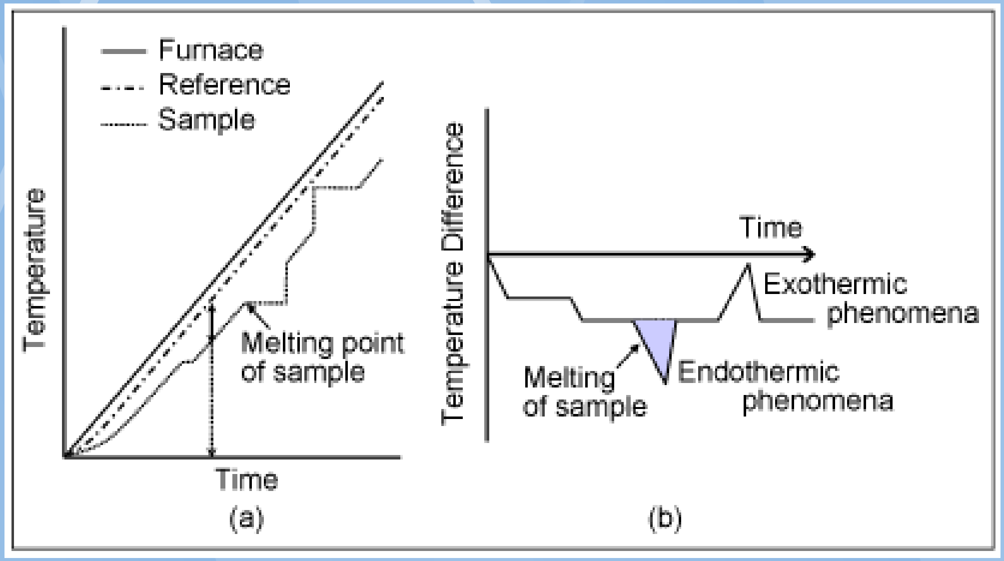
Differential thermal analysis

(Diferenciální termická analýza)

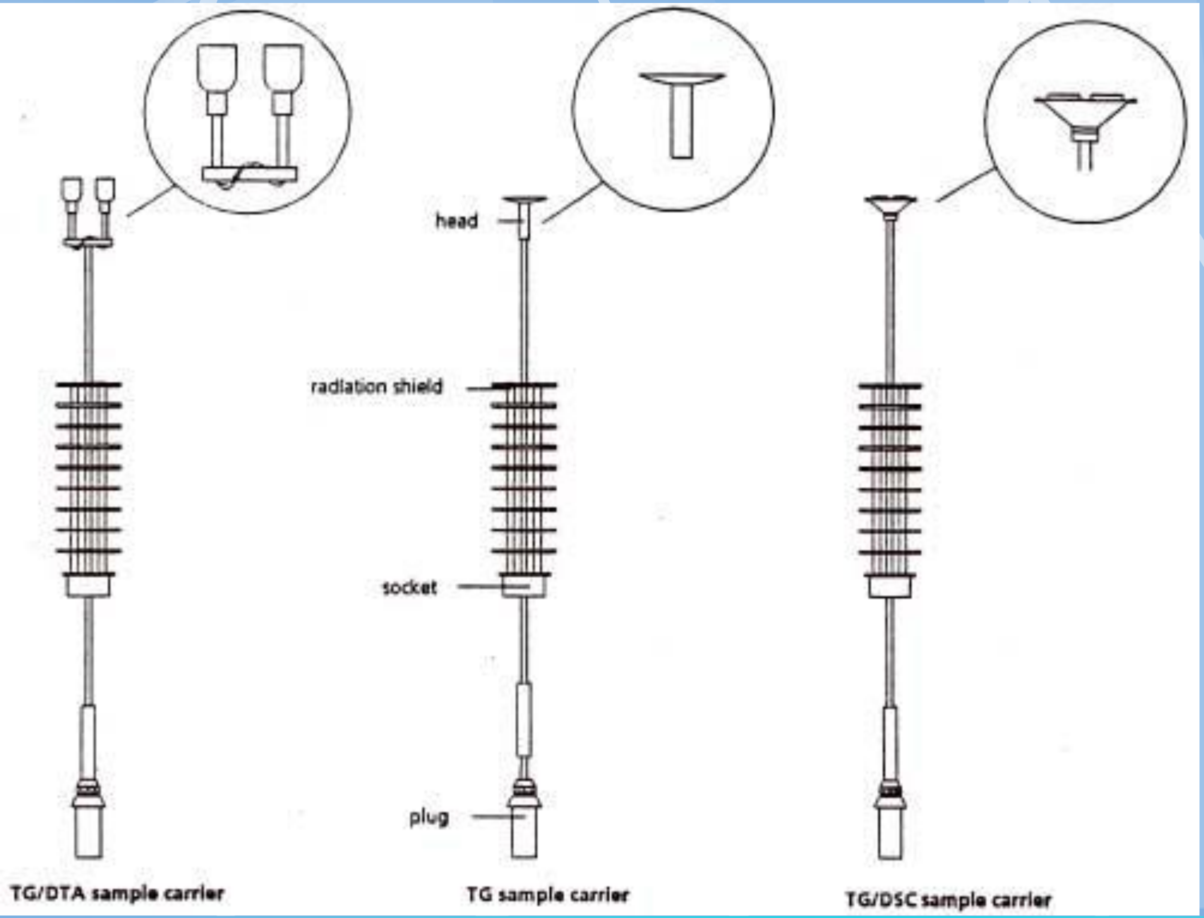
ICTAC definice DTA

A technique in which the difference in temperature between the sample and a reference material is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed.



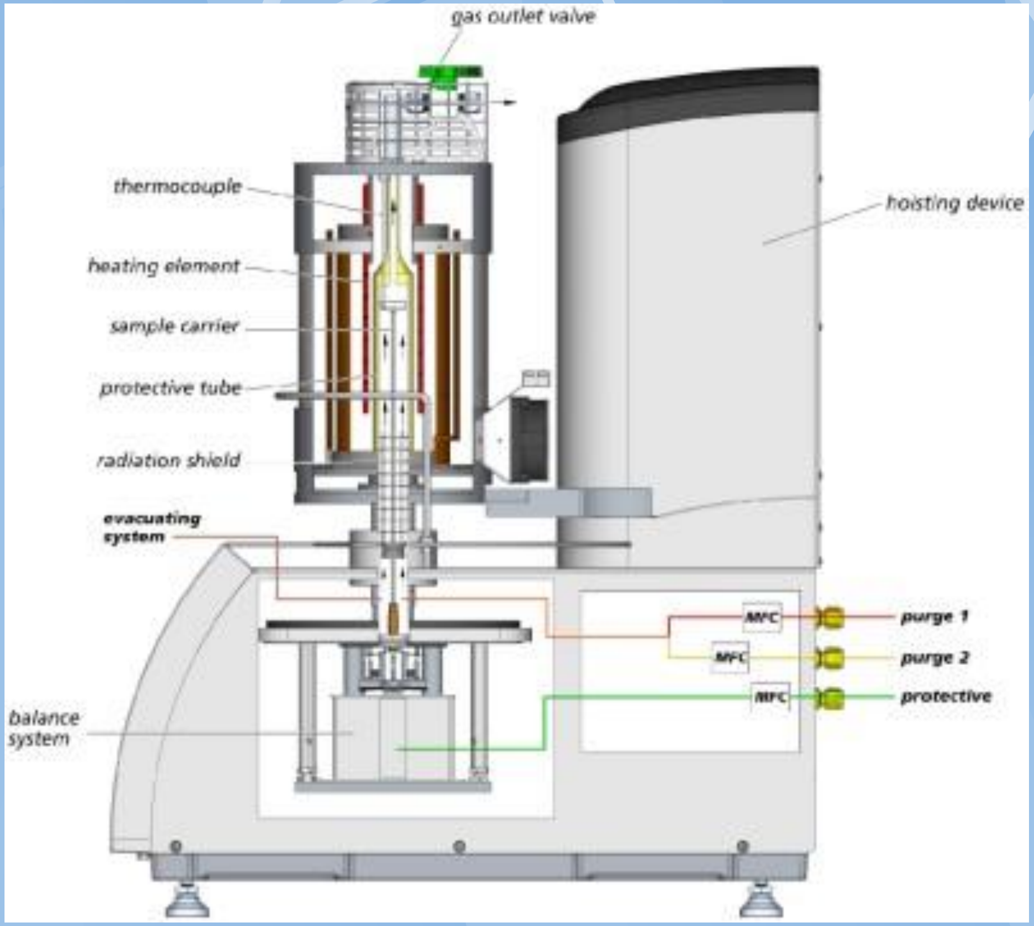


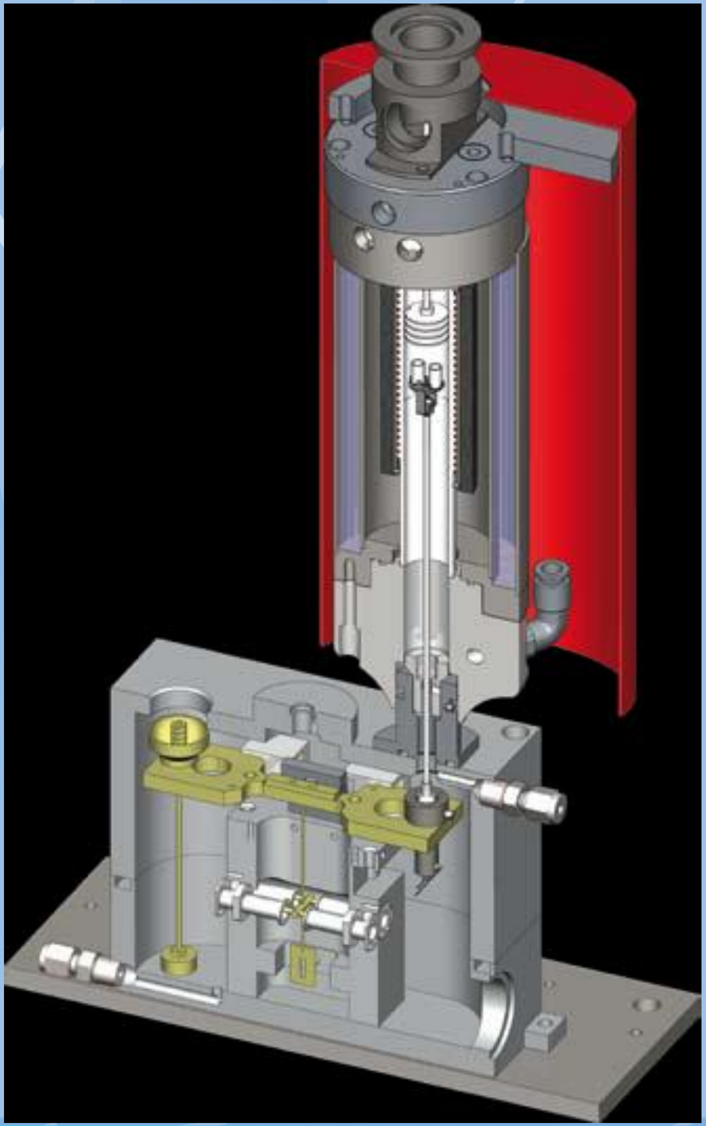
Výměnné držáky hfDSC a DTA



http://www.vestnikverejnychzakazek.cz/cs/Form/Display/318931(výběrové řízení)

STA Netzsch vs. STA Setaram





Netzsch

http://www.setaram.com/LABSYS-evo.htm

Rozdíl v citlivosti

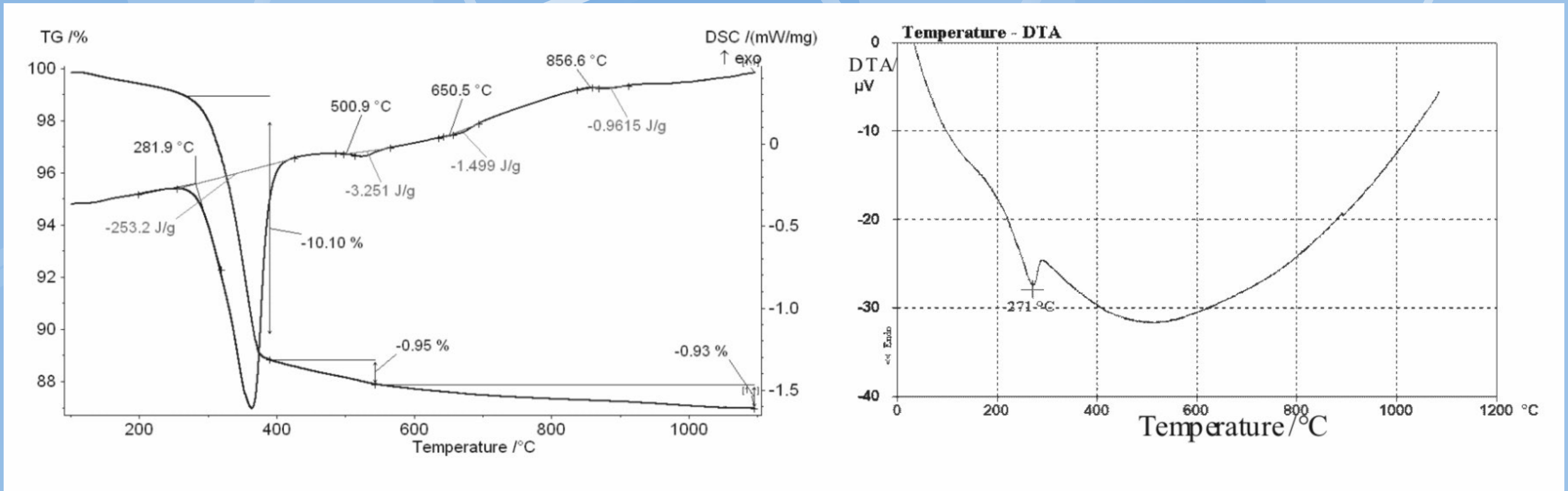
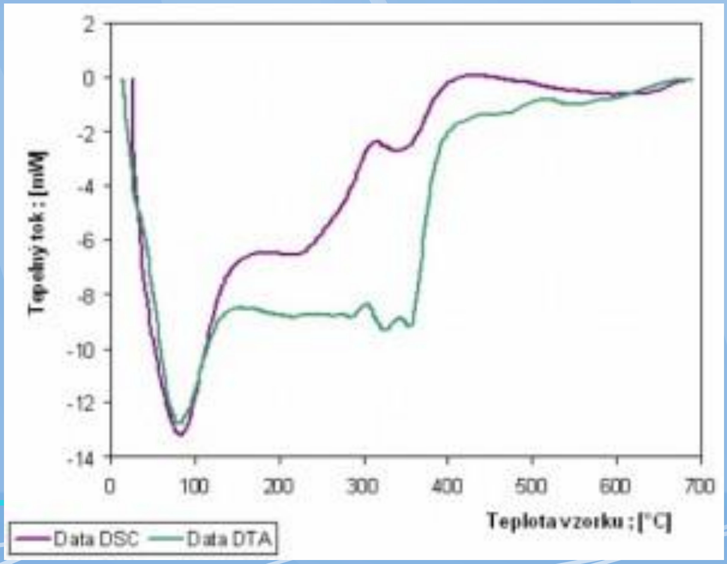
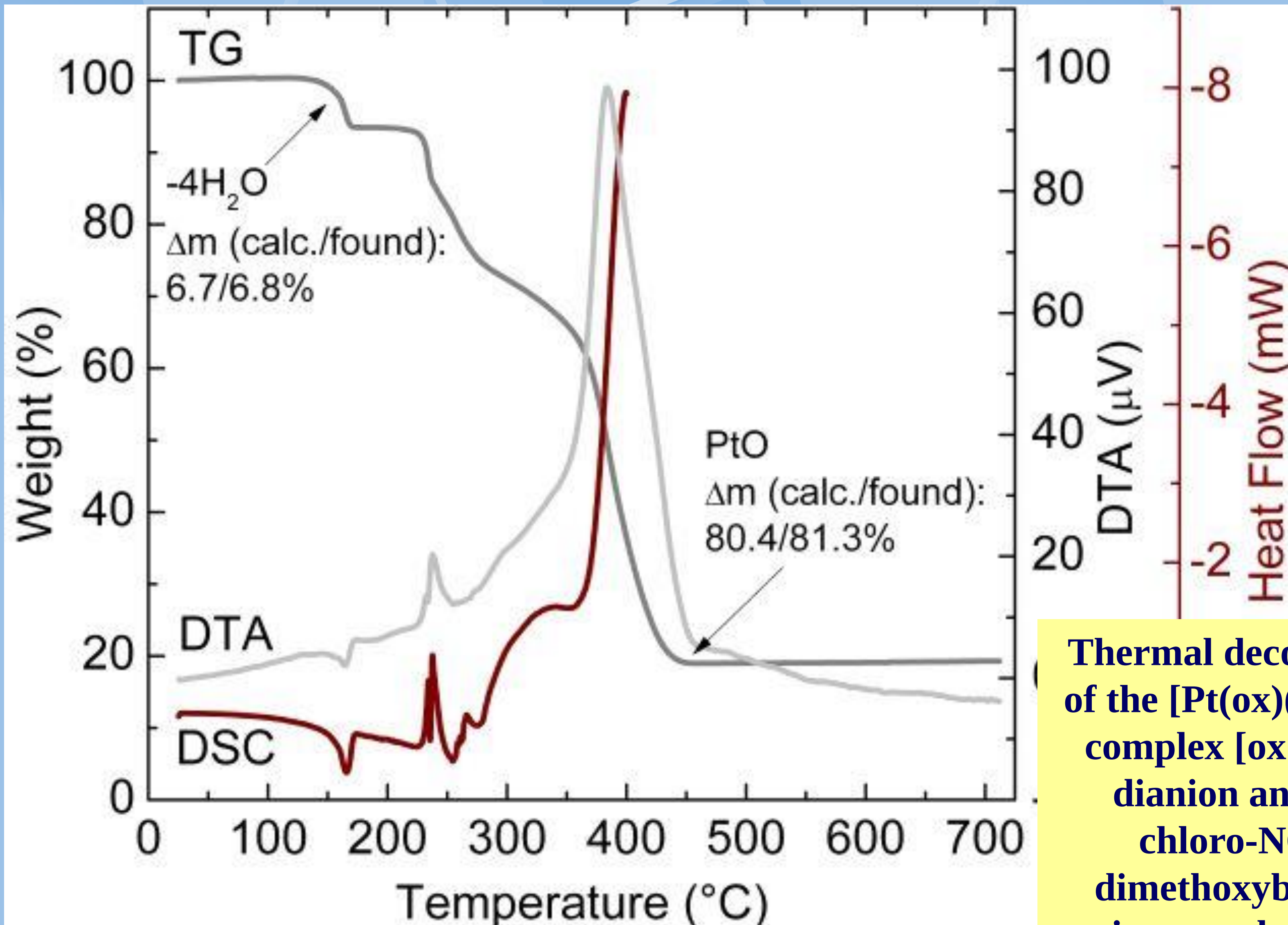


Figure 3. hfDSC/TG heating curve (a) and DTA heating curve for the limonite(b)

Pyrolýza biomasy:

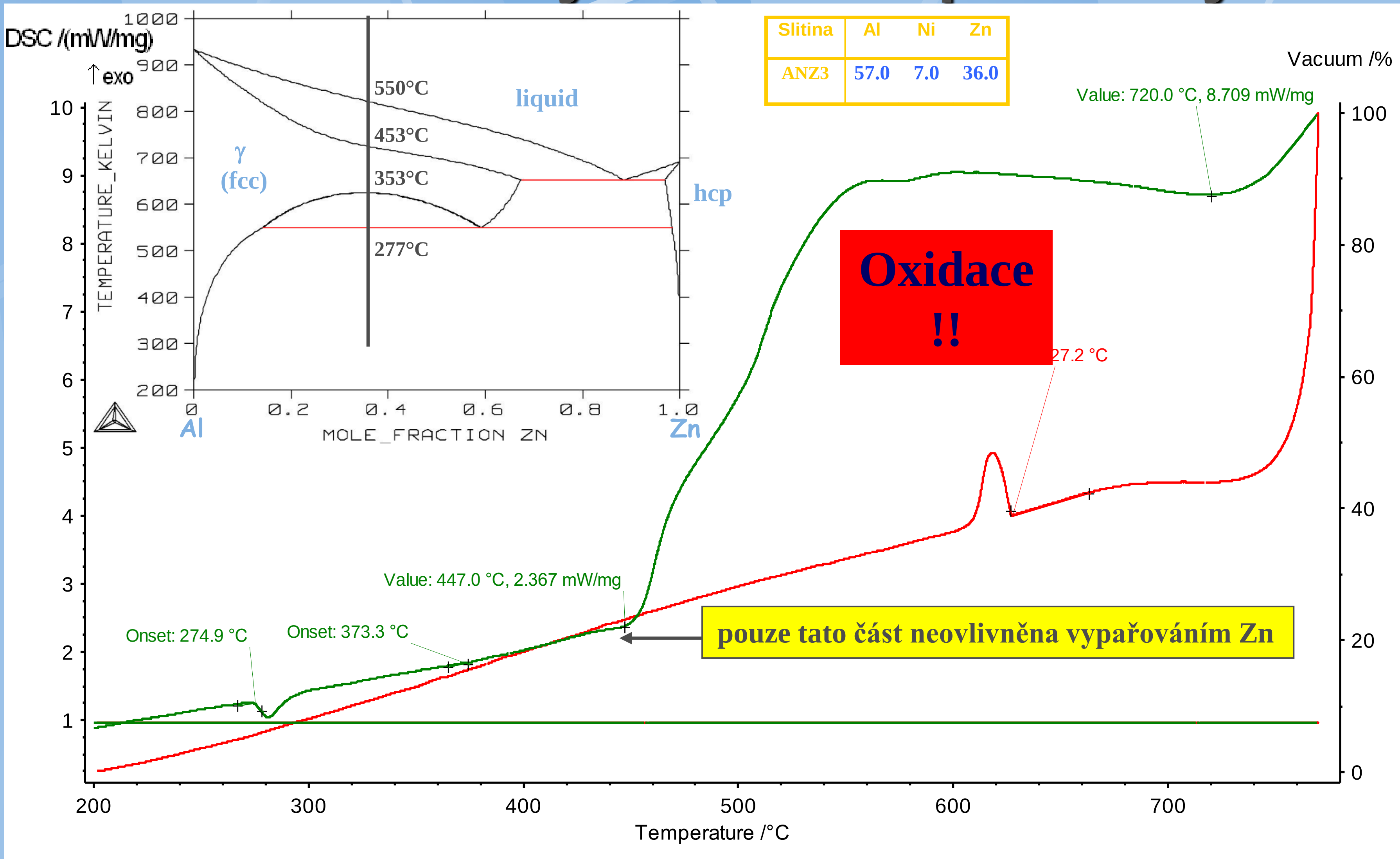


Porovnání pcDSC a DTA



Thermal decomposition of the $[Pt(ox)(L)_2]\cdot 4H_2O$ complex [ox = oxalate dianion and L = 2-chloro-N6-(2,4-dimethoxybenzyl)-9-isopropyladenine].

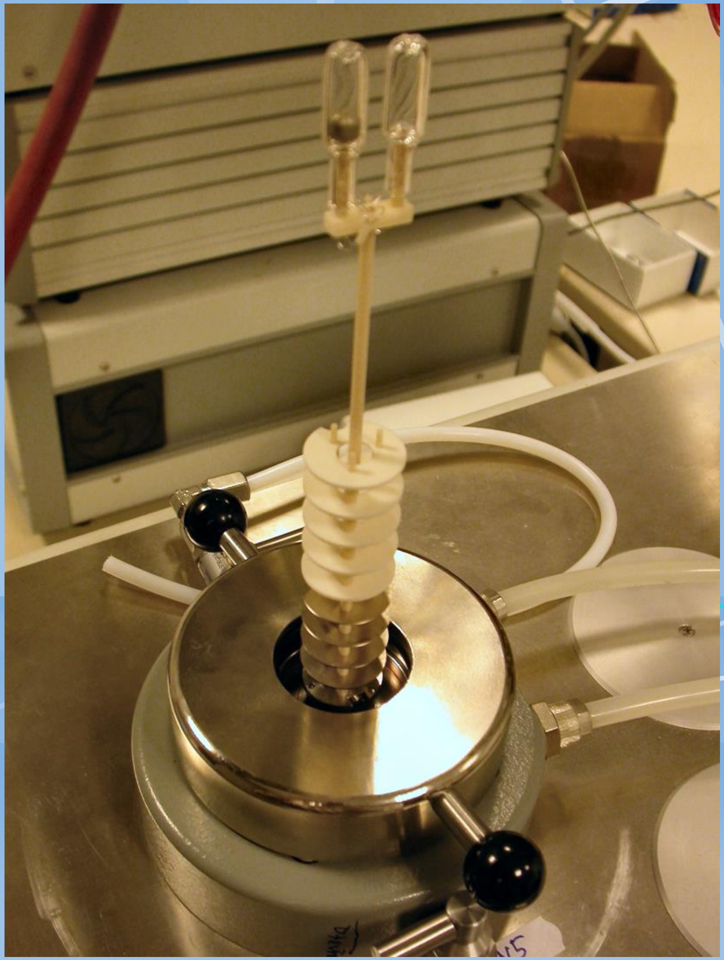
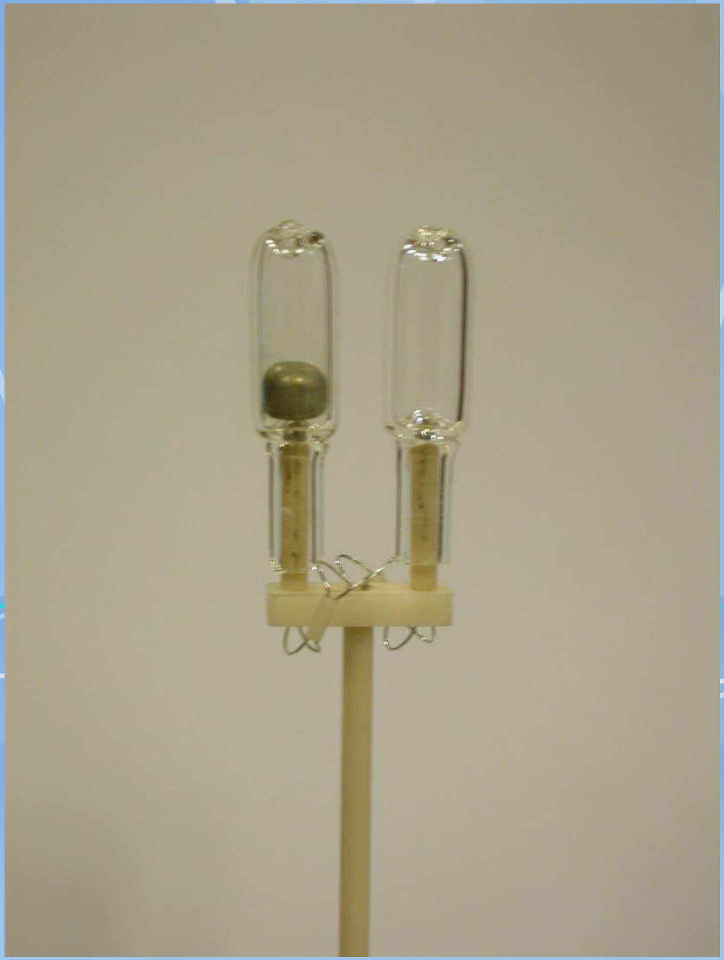
Termická analýza – DSC - problémy



Slitina	Al	Ni	Zn
ANZ3	57.0	7.0	36.0

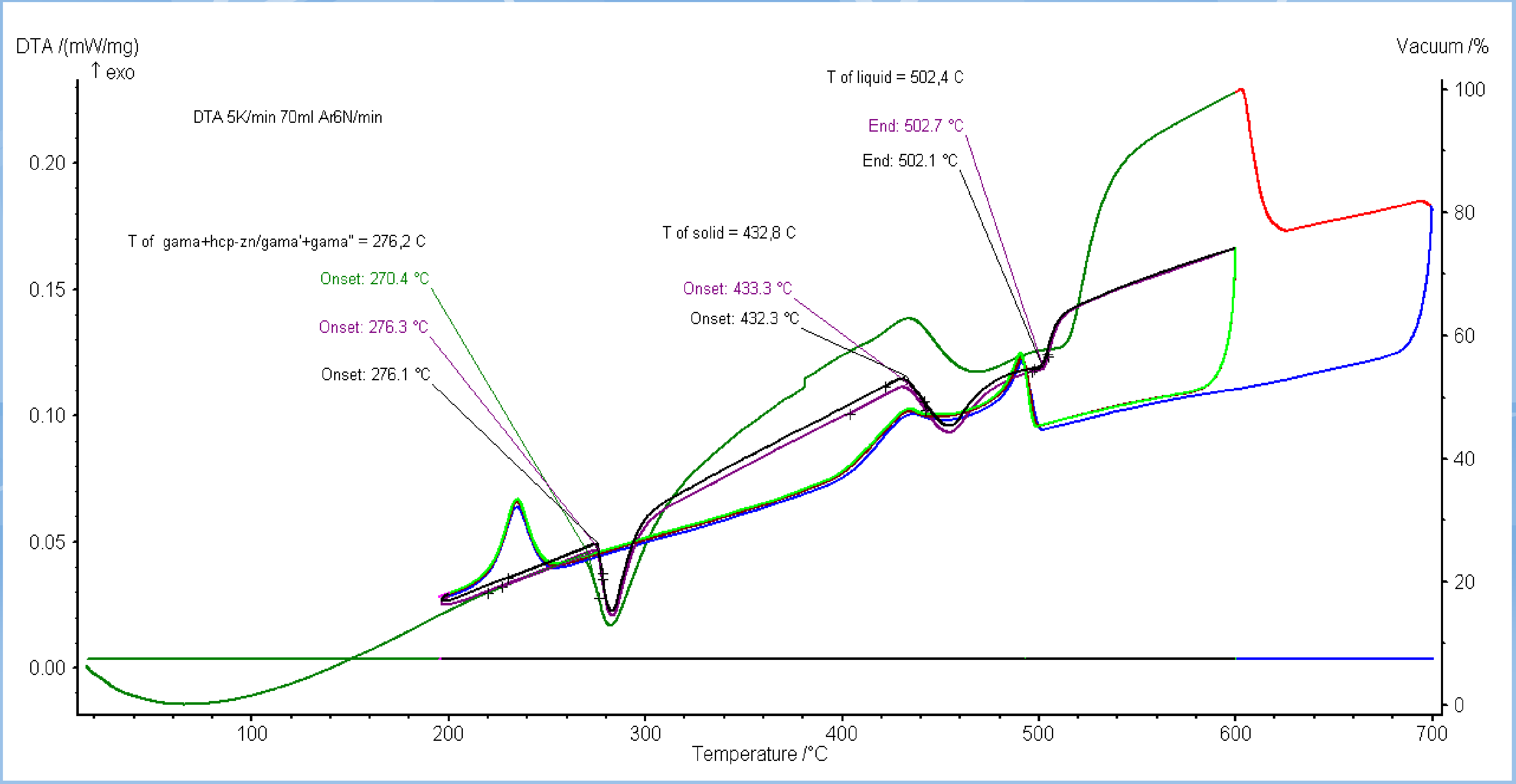
Vyhodnocení DSC křivek pro vzorek ANZ3

DTA Ampule pro STA 409 Netzsch


Měření standardu a vzorku v křemenné ampuli (Sn a ANZ1)

DTA Termická analýza v křemenných ampulích



Vyhodnocení DTA křivek pro vzorek ANZ3

Použití Ampulí pro DTA

Výhody:

•bezpečnost, odolnost proti oxidaci, vhodné pro snadno těkavé kovy a jejich slitiny (Zn, Mn, Cd,…),…necitlivost k nosnému plynu, …

•reprodukovatelnost při vícenásobných ohřevech, teplotní přesnost srovnatelná s DSC, …..

•! Možnost použít ampule pro dlouhodobé izotermní žíhání.

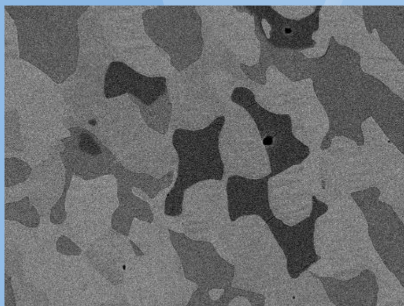
Nevýhody:

•menší citlivost,…

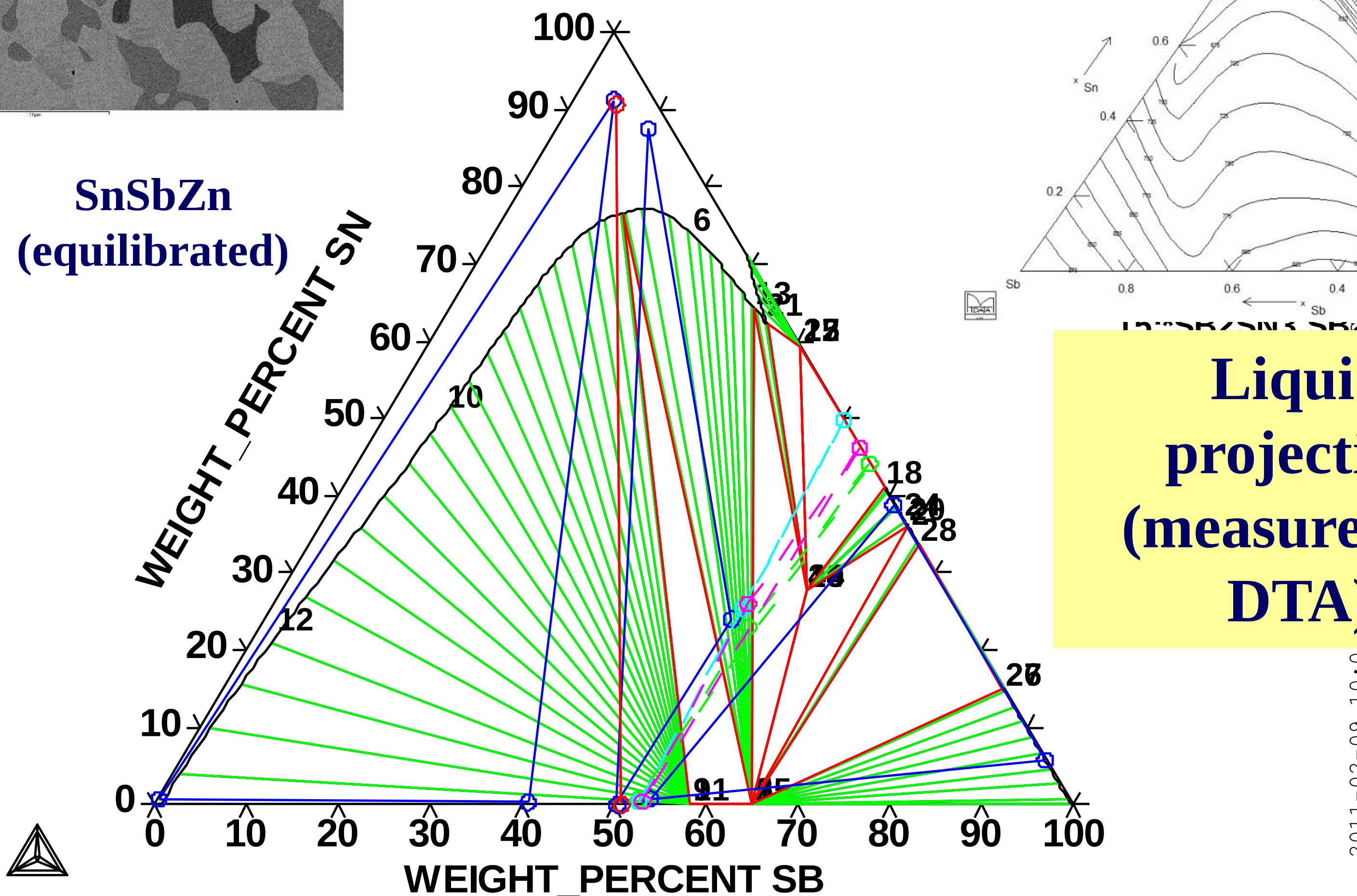
•Do cca 1100stC

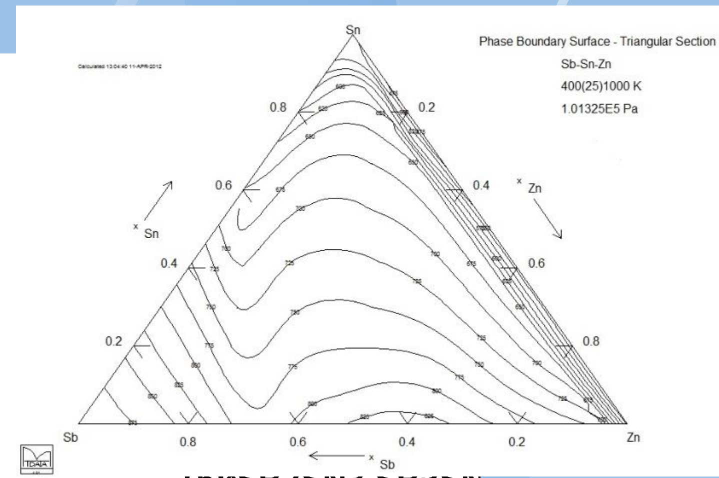
Existují křemenné ampule i pro DSC.

FD- Use of isothermal heating + DTA



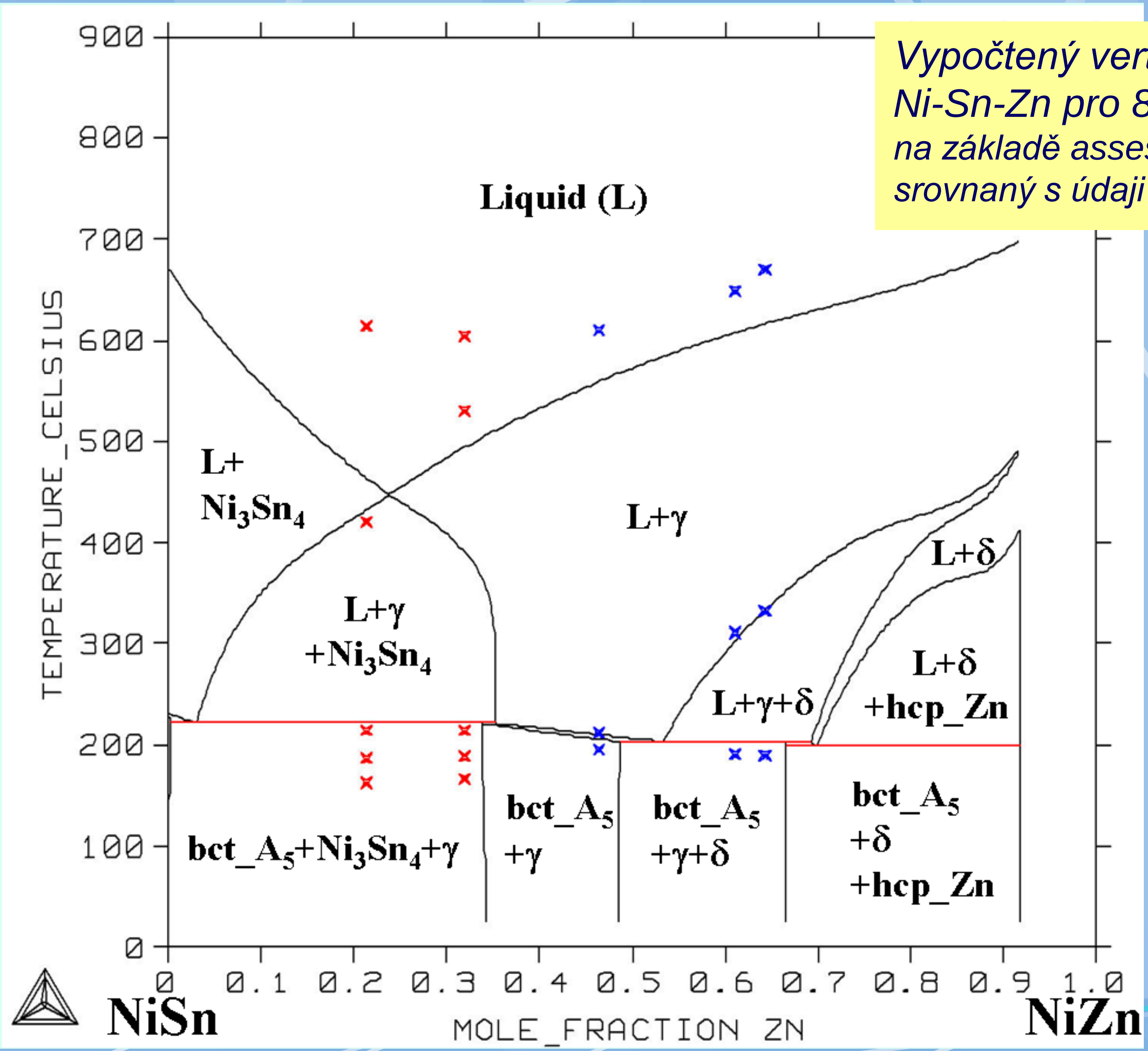
SnSbZn
(equilibrated)





Liquid projection (measured by DTA)

Sestavení fázových diagramů



Vypočtený vertikální řez soustavou
Ni-Sn-Zn pro 8.3 at.% Ni
na základě assessmentů pro binární soustavy
srovnaný s údaji z termické analýzy DTA

DTA - Žáropevné oceli

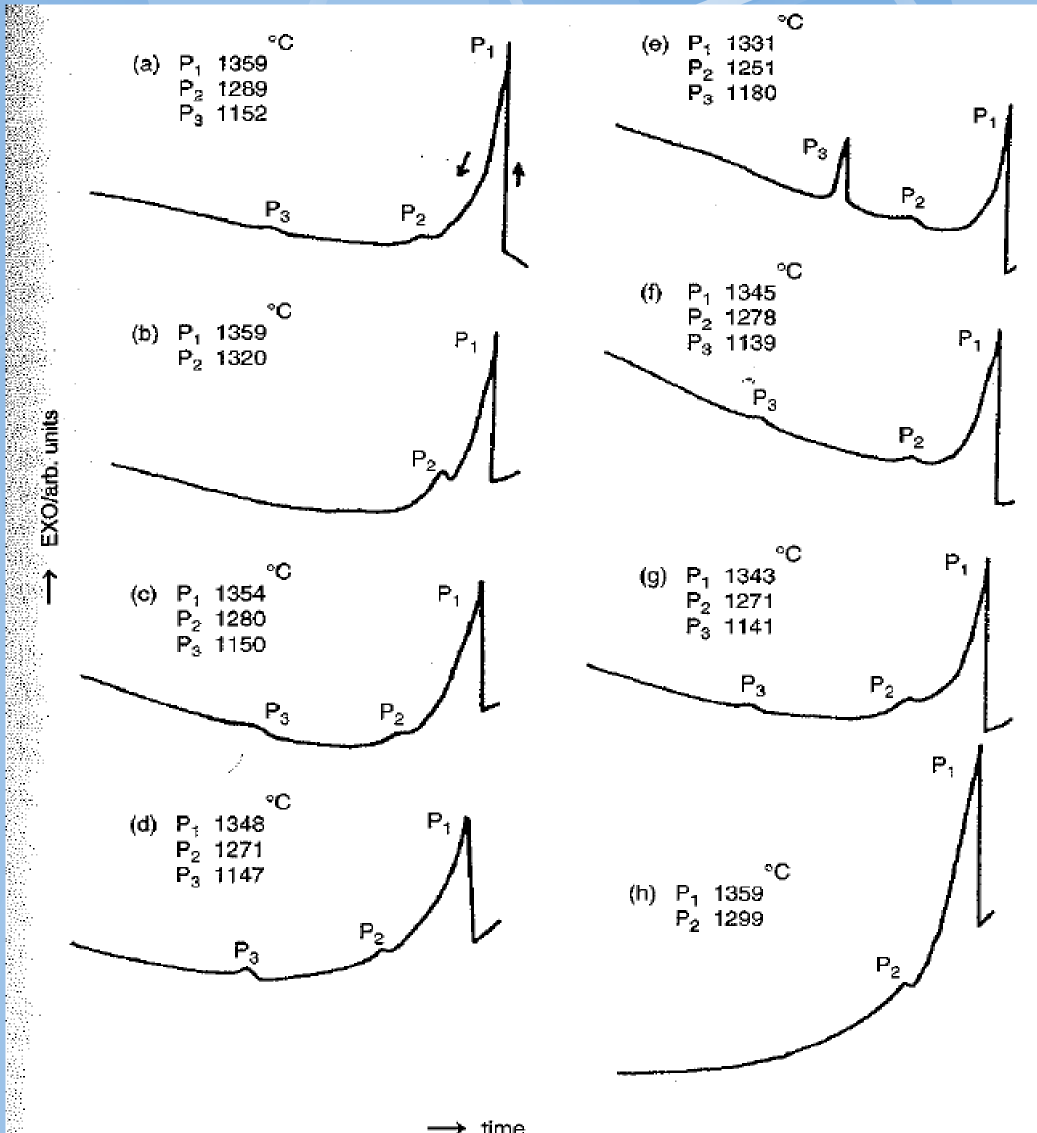
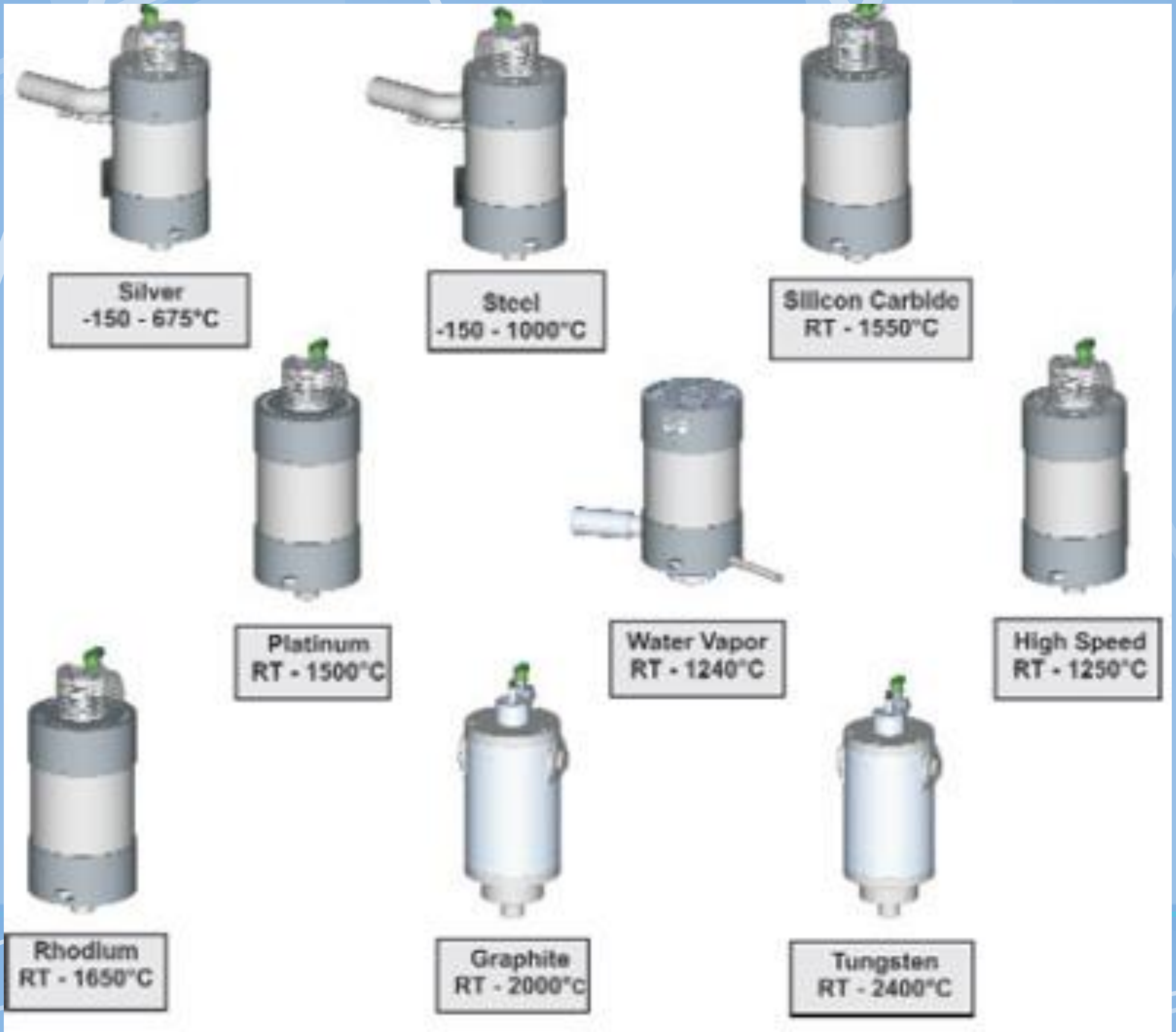


Figure 1 DTA curves of Inconel 718 alloy itself and Inconel 718 alloys containing small amounts of various additive elements subjected to continuous cooling from liquid: (a) master alloy; (b) + 0.04 mass% C; (c) + 0.5 mass% Nb; (d) + 1.0 mass% Nb; (e) + 2.0 mass% Nb; (f) + 0.2 mass% Al; (g) + 1.0 mass% Mo; (h) + 0.5 mass% Ti

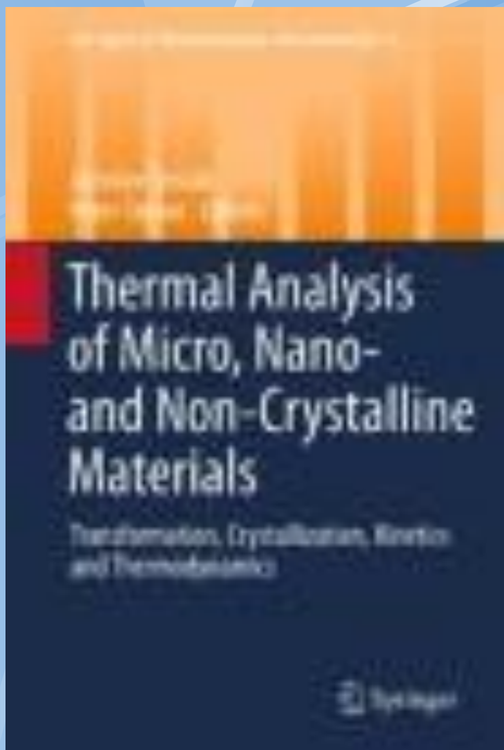
Master alloy + přídavky různých legur (C,Nb,Al,Mo, Ti)

Pracovní rozsahy pecí



Pro vysoké teploty je lepší DTA

Phase Transition in DTA



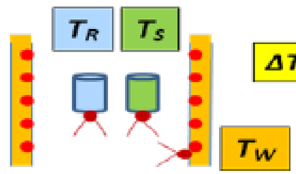


Fig. 5.1 Arrangement of the sample (S) and reference (R) holders with respect to the furnace wall.

Šesták, Sedmidubský: Heat Transfer and Phase Transition in DTA Experiments | SpringerLink

Full text: Heat Transfer and Phase Transition in DTA Experiments (researchgate.net)

5.2 DTA equation and its testing by rectangular heat pulse

Starting from the analysis of the heat transfer process under the conditions of DTA apparatus and using ideas of Faktor & Hanks [47] the simple balances of heat fluxes for sample and reference holders were found [49, 50]:

3 1 2

Sample holder: $$K_S(T_W - T_S) = C_P^S(\mathrm{d}T_S/\mathrm{d}t) - \Delta_t H(\mathrm{d}\xi/\mathrm{d}t) \quad (5.1)$$

Reference holder: $$K_R(T_W - T_R) = C_P^R(\mathrm{d}T_R/\mathrm{d}t) \quad (5.2)$$

where K_S, K_R are the coefficients of heat transfer between the furnace wall (with temperature T_W) on one side and the sample holder (with temperature T_S) and the reference holder (with temperature T_R) on the other side, respectively; C_P^S and C_P^R are the heat capacities of sample holder (including sample) and reference holder (including reference material); $\Delta_t H$ is the enthalpy change of phase transition (positive for endothermic process) and $\mathrm{d}\xi/\mathrm{d}t$ is the rate of the transition (ξ is the progress variable or extent of transition and t means time).

From the balances, the DTA equation (expressing temperature difference ΔT_{DTA} between the sample and the reference holders) was derived in the form:

$$\boxed{\Delta T_{DTA} = \frac{1}{K_{DTA}}\left(\Delta K(T_W - T_R) - (C_P^S - C_P^R)\Phi - C_P^S\frac{\mathrm{d}\Delta T}{\mathrm{d}t} + \Delta_t H\frac{\mathrm{d}\xi}{\mathrm{d}t}\right) \quad (5.3)}$$

where $\Delta T_{DTA} = T_S - T_R$; $\Delta K = K_S - K_R$; $\Phi = \mathrm{d}T_R/\mathrm{d}t$ (linear heating rate); $K_{DTA} = K_R$ („apparatus constant“ of DTA depending on temperature T_R and heating rate Φ).

The heat capacity of sample C_P^S can be expressed as depending on the extent of transition ξ

$$C_P^S = C_{P\,\mathrm{in}}^S + \xi\,\Delta_t C_P^S \quad (5.4)$$

where $C_{P\,\mathrm{in}}^S$ is the initial heat capacity of sample (including sample holder) and $\Delta_t C_P^S$ is the heat capacity change due to transition, for which Person–Kirchhoff equation is valid:

$$\Delta_t C_P^S = \left(\frac{\partial \Delta_t H}{\partial T}\right)_P$$

Cp a ΔH lze vypočítat metodou Calphad

1… rychost s jakou přijímá vzorek teplo při ohřevu (heat flux)

2… rychost s jakou přijímá vzorek teplo při procesu fázové transformace v rozsahu ζ

3… rychost s jakou je předáváno teplo ze stěn vzorku

Vzorek je poněkud „netečný“ (inertní) k ohřevu tím, že se část tepla pohlcuje fázovou transformací.

[What is Thermal Inertia? - YouTube]

„vzdorování ohřevu“

Stabilized temperature profile in homogeneous substance at linear heating (cylindrical approximation)

8 **V jednoduché parabolické aproximaci**

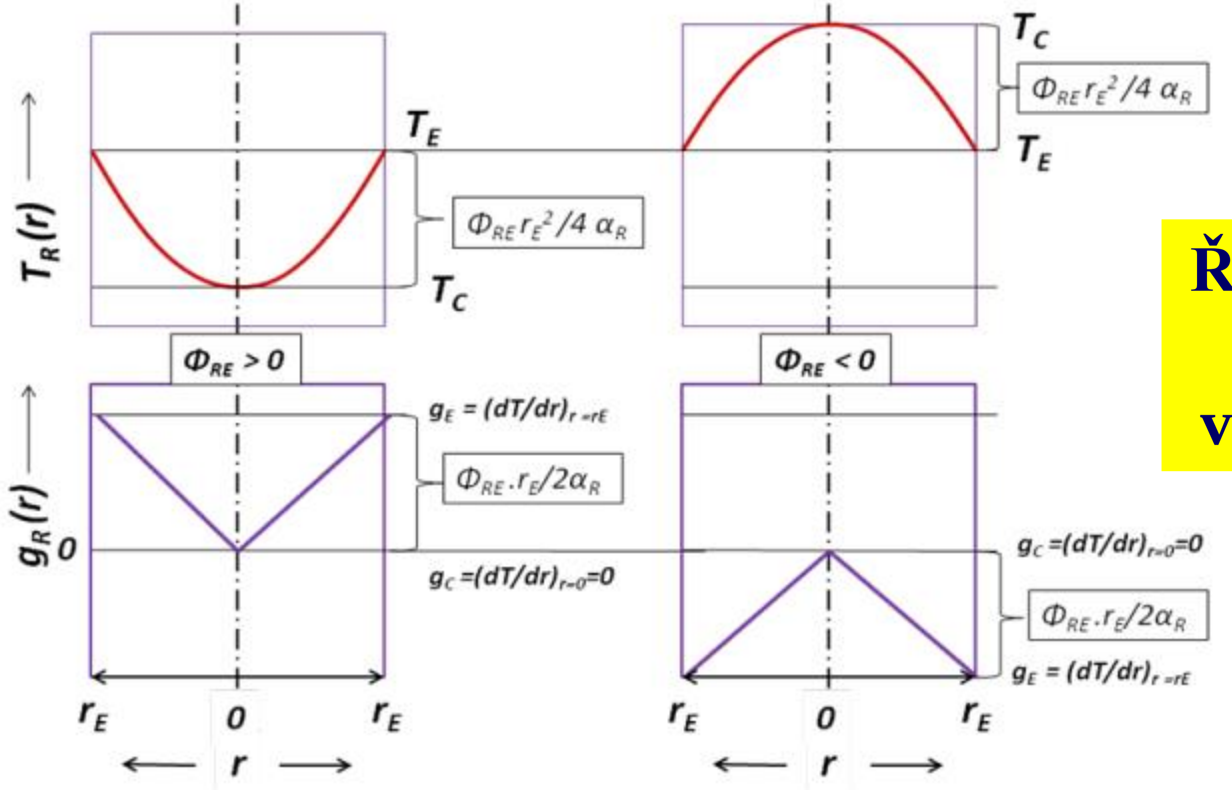
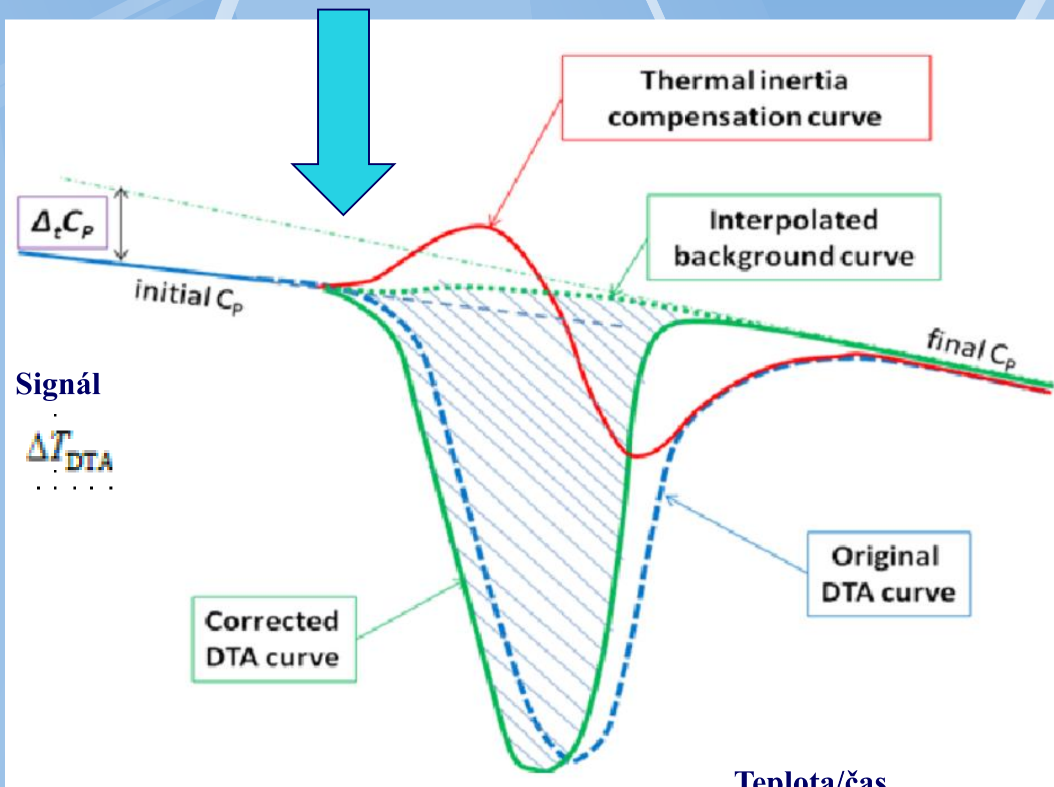


Fig. 5.5 Stabilized temperature profile $T_R(r)$ and gradient profile $g_R(r)$ at linear heating ($\Phi_{RE} > 0$) and linear cooling ($\Phi_{RE} < 0$) in infinite cylinder with external radius r_E.

Řešení problému: použít malý vzorek (viz DSC)

Důsledky pro DTA signál

počátek fázové transformace (např. tání)



2 Correction of DTA curve with respect to thermal inertia

Za počátek však z exp. důvodů považujeme graficky vyhodnocené body „on sety“. V “Africe“ pak používají minima peaků

DTA equation and its testing by rectangular heat pulse

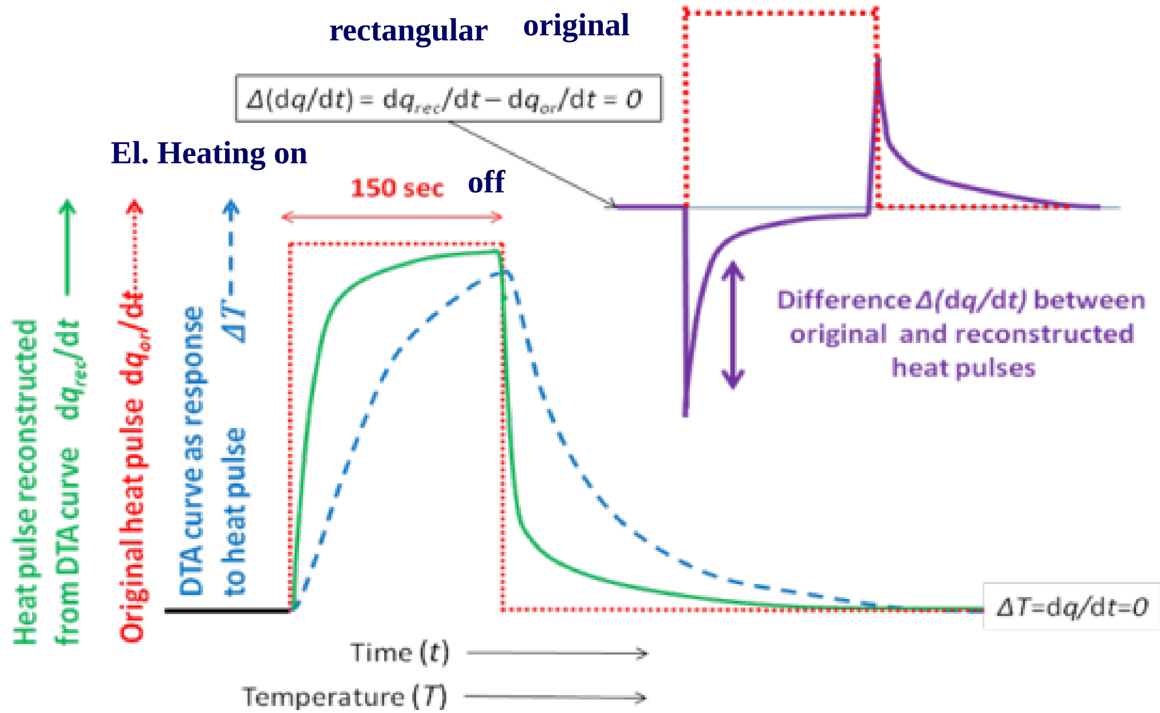


Fig. 5.3 Use of DTA equation (5.3) for reconstructing the heat pulse from DTA curve as a response to artificial rectangular heat pulse [52]. The greatest differences between the original and reconstructed heat process is in the fields near to the onset and the end of rectangular pulse, where the heat flux is abruptly changed ($\ddot{q} \equiv d^2q/dt^2 \rightarrow \pm\infty$).

Temperature profile in a sample exhibiting first-order phase transition

Consider a sample in the form of infinite cylinder with external radius r_E. The sample exhibits an endothermic first-order phase transition with the equilibrium transition temperature T_t and molar enthalpy change $\Delta_t H_m$. During the transition, the initial phase φ_i with molar volume V_m^i, molar heat capacity $C_{P,m}^i$ and heat conductivity λ_i is changed into the final phase φ_f with the respective quantities V_m^f, $C_{P,m}^f$ and λ_f. The overall extent of transition ξ_G is determined as fraction of molar amount of the final phase N_f (molar amount of the transformed part of sample) referred to the whole sample:

$$\xi_G = \frac{N_f}{N_i + N_f} \qquad (5.37)$$

where N_i is molar amount of the nontransformed part of sample (molar amount of remaining initial phase).

To avoid the problems of changing radius due to molar volume change at the transition, it is assumed that the transition does not change the sample volume: $V_m^i = V_m^f$; $\Delta_t V_m = 0$.

When the sample is exposed to a linear heating then four stages can be distinguished with respect to the temperature profile inside the sample.

I. Temperature at any part of the sample is lower than the (equilibrium) transition temperature $T_t > T$ so that the stabilized temperature profile occurs inside the sample in the form

$$T_i(r) = T_{SE} - \frac{\Phi_{RE}}{4\alpha_i}(r_E^2 - r^2) \qquad (5.38)$$

where $\alpha_i = \lambda_i V_m^i / C_{P,m}^i$ represents the thermal diffusivity of the initial phase φ_i, T_{SE} is the temperature detected on the sample surface and $\Phi_{RE} \approx dT_{SE}/dt$ is the applied linear heating rate.

II. Temperature higher than T_t in a part of the sample, the phase transition is in progress and the extent of transition inside the whole is lower than unity ($0 < \xi_G < 1$). The temperature profile is not stabilized since it is affected by a „heat sink“ heat due to the running endothermic transition.

III. Temperature at any part of the sample is higher than T_t and the extent of transition is equal to unity; however, the temperature profile is not yet stabilized but it is tending to reach the stabilized state.

IV. The stabilized temperature profile after the transition is reached in the form:

$$T_f(r) = T_{SE} - \frac{\Phi_{RE}}{4\alpha_f}(r_E^2 - r^2) \qquad (5.39)$$

where $\alpha_f = \lambda_f V_m^f / C_{P,m}^f$ represents the thermal diffusivity of the final phase φ_f.

The thermal behaviour of the sample upon the transition can be approached using two different models; a continuous and a discontinuous one.

Temperature profile in a sample exhibiting first-order phase transition „continuous model“

Model zahrnuje řešení rovnic difúze a fázovou transformaci

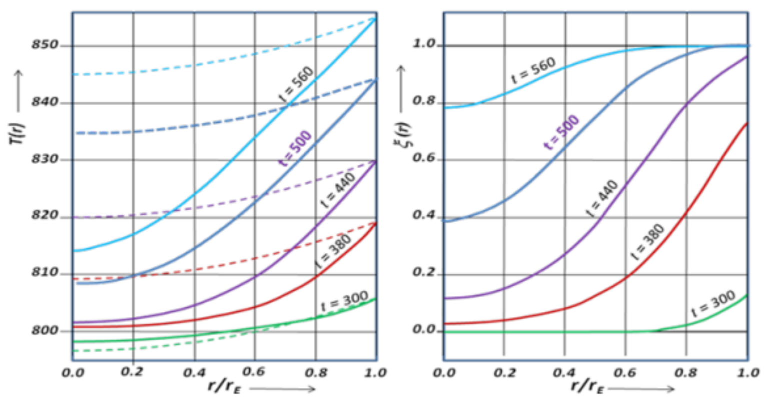


Fig. 5.8 Local temperatures $T_S(r)$ (left) and local extents of transition $\xi_r(r)$ (right) in the sample at various times according to the „continuous model“ (Eq. 5.44). The transition starts at $t = 260$ s. Dashed lines in the left part represent the stabilized profiles corresponding to the given surface temperatures (without any transition).

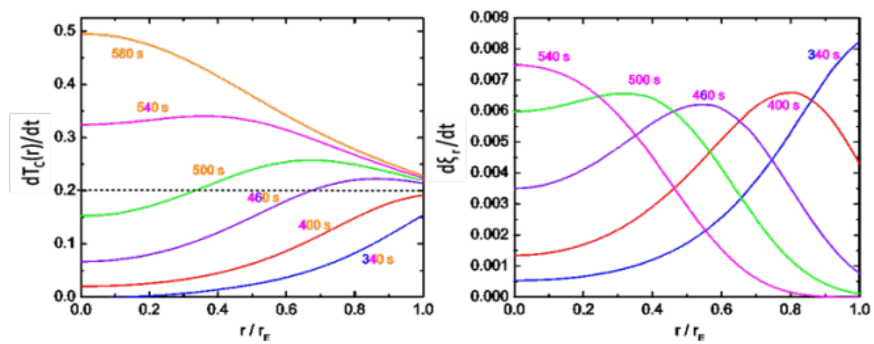


Fig. 5.9 Profiles of rates of local temperature change $dT_S(r)/dt$ (left – applied heating rate $\Phi = 0.2$ K/s as dotted line) and rates of the local extent of transition $d\xi_r(r)/dt$ (right) in the sample at various times according to the „continuous model“ (Eq. 5.44)

V oblastech, kde díky teplotě již probíhá fázová transformace (např. přeměna v tuhé fázi $\alpha \rightarrow \beta$ je její rozsah v rozmezí:

$$(0 < \xi_G < 1).$$

„Discontinuous model“ of a phase transition

Postupující fázové rozhraní

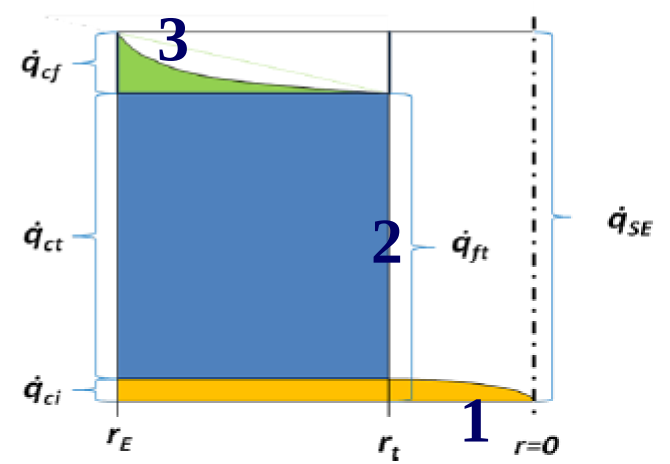


Fig. 5.13 Heat flux profiles in a cylindrical sample during transition according to discontinuous model

Ve vzorku postupuje od kraje ke středu fázové rozhraní např. $\alpha \rightarrow \beta$ při masivní transformaci. Rozsah fázové transformace ξ_G je před frontou 0 za ní 1.

Tok tepla se spotřebovává na: 1… ohřev původní fáze, 2…na přeměnu na rozhraní, 3… na ohřev nové fáze

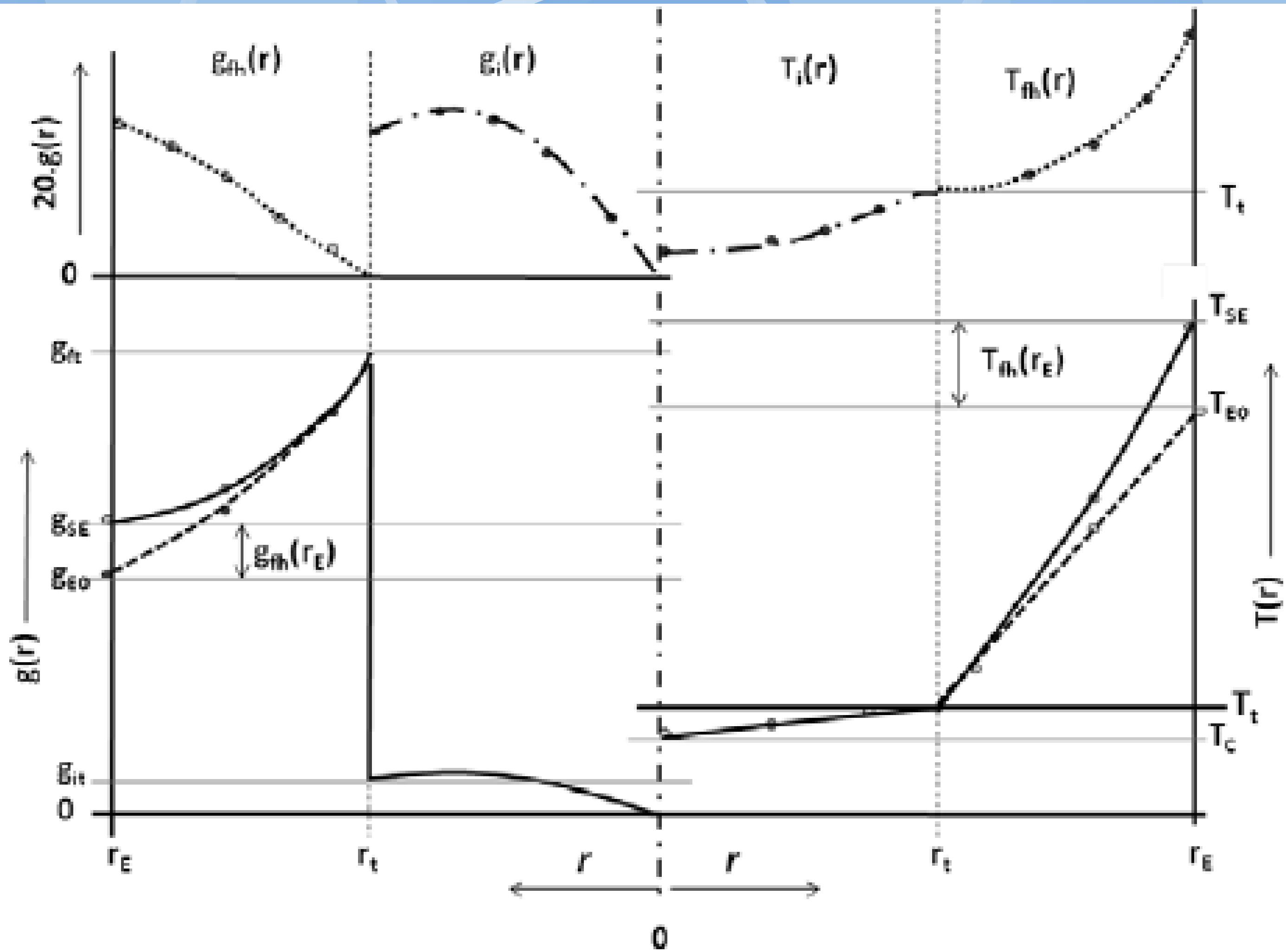


Fig. 5.14 Radial temperature gradient profile $g(r)$ (left) and local temperature profile $T(r)$ (right)

Temperature profile and temperature modulation

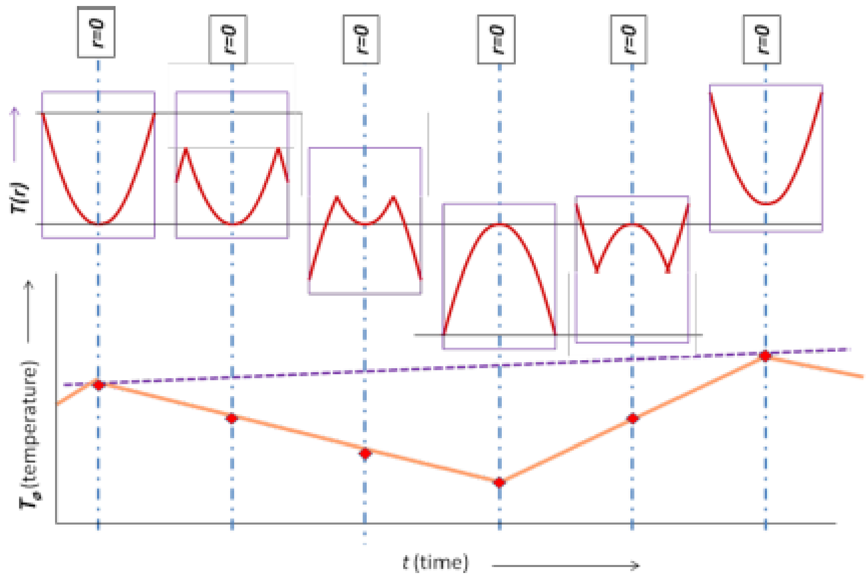


Fig. 5.15 Simplified idea of changes in te

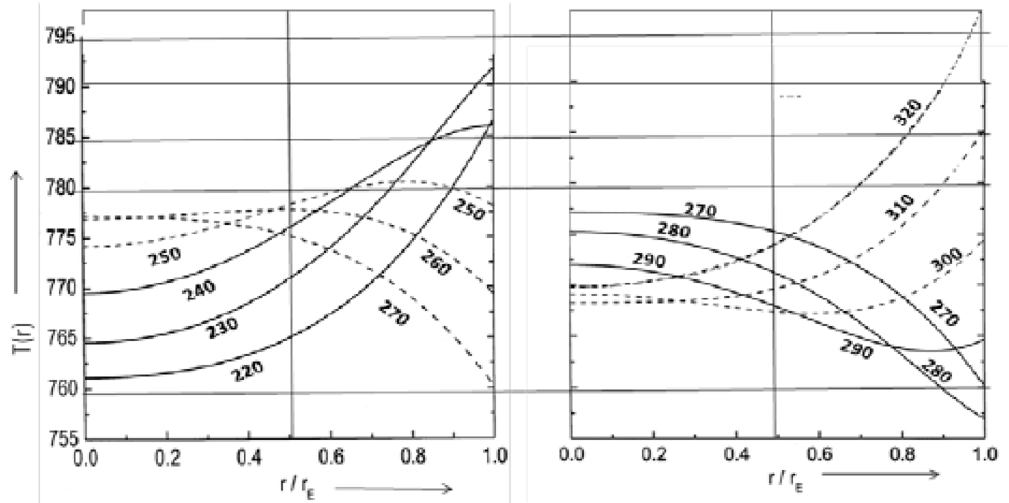


Fig. 5.16 Calculated development of temperature profile $T(r)$ during one period of temperature modulation (period $\tau = 100$ s, heating rate $\Phi = 0.1 \pm 0.6$ K/s, $a_S = 0.05$ cm^2/s, $r_E = 1$ cm) for times 220–320 second

Diskuze