

Audio test:



Termická analýza



Simulace DSC a DTA

Přednášející: Doc. Jiří Sopoušek

Obsah

- Výpočty fázových diagramů metodou CALPHAD
- Výpočet entalpie vzorku a C_p
- Simulace signálu DTA (pcDSC, hfDSC)
- Příklady použití

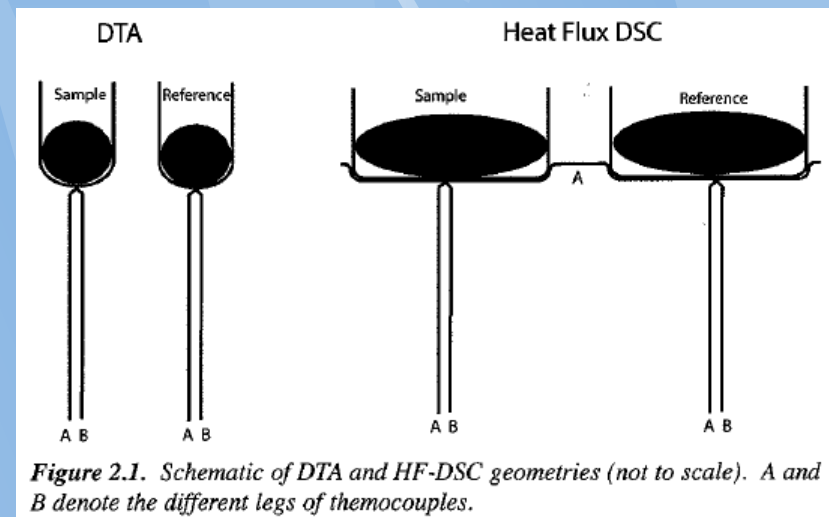


Figure 2.1. Schematic of DTA and HF-DSC geometries (not to scale). A and B denote the different legs of thermocouples.

Zdroje

[98Sau] N. Saunders, A. P. Miodovnik: '**CALPHAD** (Calculation of Phase Diagram) - A Comprehensive Guide', Pergamon Materials Series, Vol.1, Elsevier Science, Amsterdam (1998).

[02Sop] Sopoušek Jiří, Brno 2002, Fázové rovnováhy a difúzí řízené procesy ve vybraných soustavách kovů a jejich slitin (**komentář** k habilitační práci).

[06Boe] W. J. Boettinger - U. R. Kattner - K.-W. Moon - J. H. Perepezko, "**DTA and Heat-flux DSC Measurements of Alloy Melting and Freezing**", 2006, Washington, National Institute of Standards and Technology.

[07Kro] Kroupa, A.; Dinsdale, A. T.; Watson, A.; Vrestal, J.; Vizdal, J.; Zemanova, A.: The development of the **COST 531** lead-free solders thermodynamic database, JOM, 2007, 59, 20-25.

CALPHAD (viz kurs Dr. Kroupa)

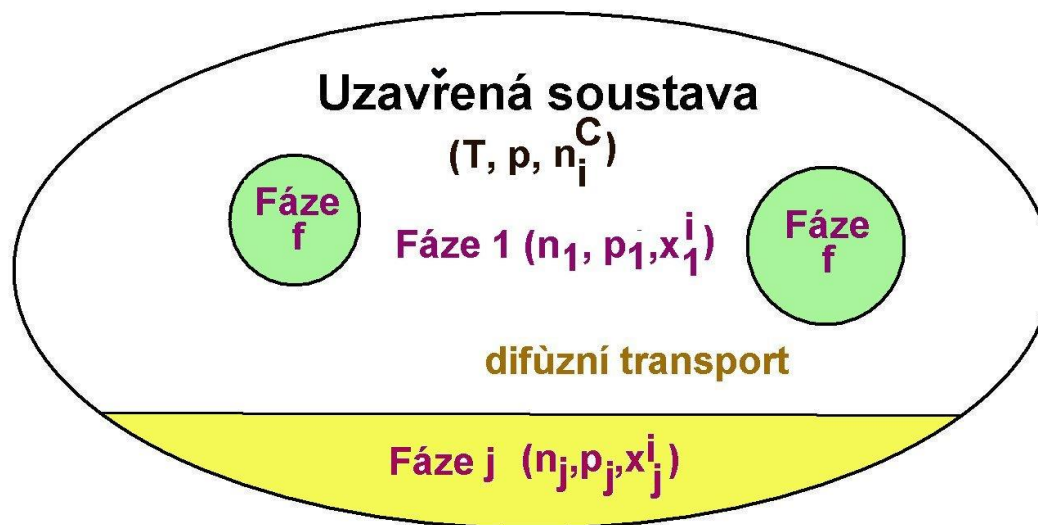
- semiempirická metoda, řešení fázové rovnováhy pro uzavřený systém

$$\begin{aligned}T_{\text{ex}} &= T \\ p_{\text{ex}} &= p \\ dn_i &= 0\end{aligned}$$

$j=1,\dots,f$ (fáze)

$i=1,\dots,s$ (složky)

Okolí

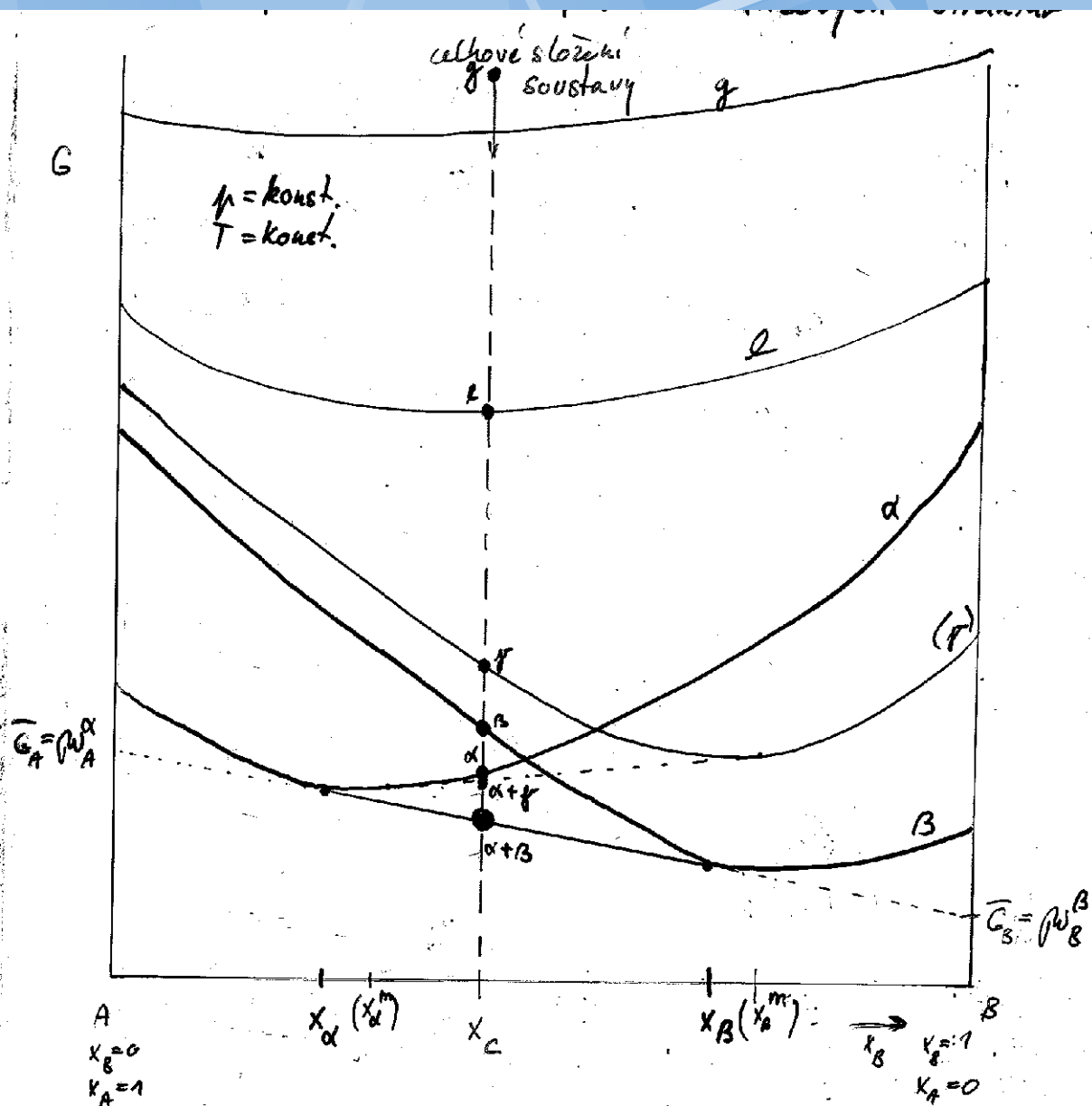


Nutný
termodynamický
popis fází:
 $G_j = f(T, p, x_j^i)$

SW a
termodyna
-mická
databáze

Nerovnovážný stav → rovnovážný stav (řešení FR)

Proč vzniká fázová rovnováha?



K získání řešení používáme:

- integrální podmínku FR (min. Gcelk)
- Diferenciální podmínku FR (rovnost chem. pot.)

Při hledání řešení dodržujeme:

- zákon zachování hmoty
- Stechiometrii fází
- zachování náboje

Řešení fázové rovnováhy

Output from POLY-3, equilibrium = 1, label A0 , database: SOLDER

Conditions:

T=473, P=100000, N=1, W(PB)=1E-1

DEGREES OF FREEDOM 0

Temperature 473.00, Pressure 1.000000E+05

Number of moles of components 1.00000E+00, Mass 1.24006E+02

Total Gibbs energy -2.59971E+04, Enthalpy 7.62867E+03, Volume 0.00000E+00

Component	Moles	W-Fraction	Activity	Potential	Ref.stat
PB	5.9848E-02	1.0000E-01	1.7267E-04	-3.4074E+04	SER
SN	9.4015E-01	9.0000E-01	1.5344E-03	-2.5483E+04	SER

BCT_A5 Status ENTERED Driving force 0.0000E+00

Number of moles 6.7295E-01, Mass 8.0858E+01 Mass fractions:

PB 2.81641E-02 SN 9.71836E-01

Constitution:

PB 1.63324E-02 SN 9.83668E-01

LIQUID Status ENTERED Driving force 0.0000E+00

Number of moles 3.2705E-01, Mass 4.3148E+01 Mass fractions:

PB 2.34618E-01 SN 7.65382E-01

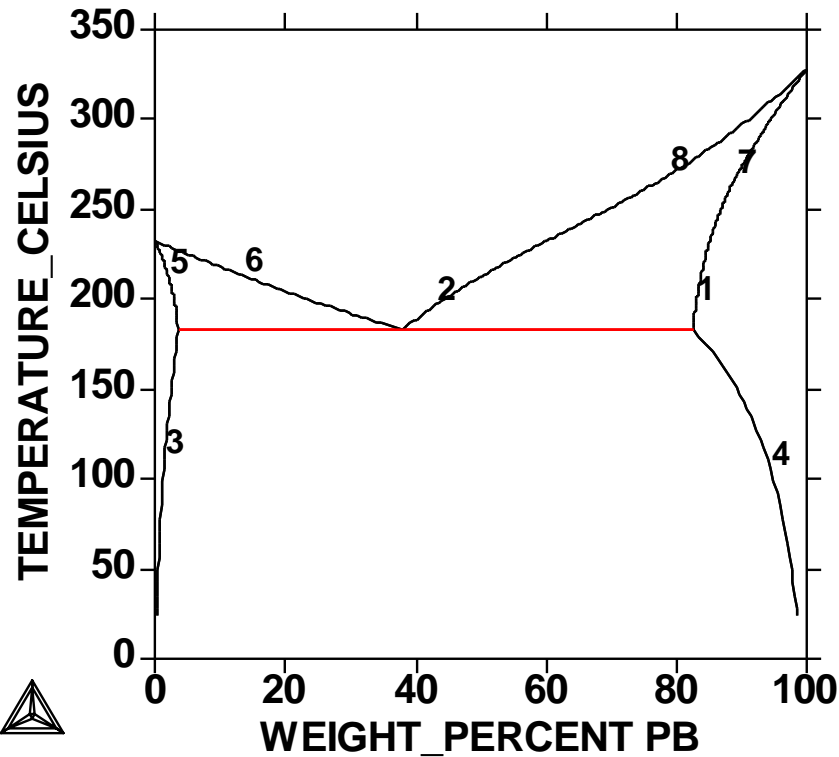
Constitution:

PB 1.49387E-01 SN 8.50613E-01

Entalpie
pro DTA
(DSC)

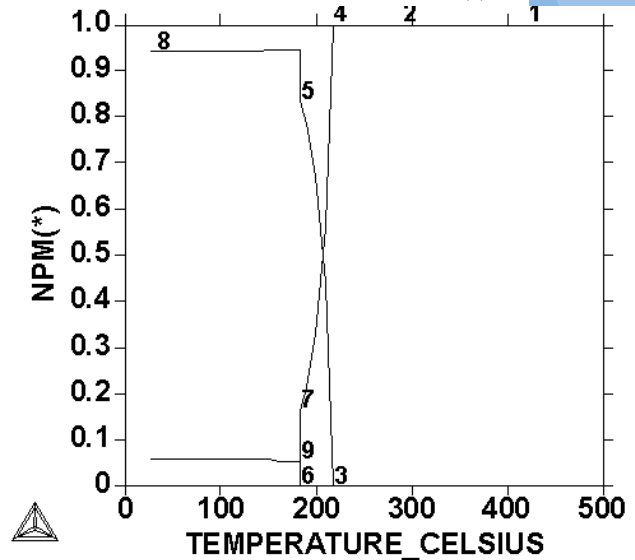
Sn-Pb

THERMO-CALC (2012.05.31:13.03) :Phase diagram PbSn
 DATABASE: SOLDER
 P=100000, N=1;



1	:	F	C	C	-	A1	L	I	Q	I	D	
2	:	F	C	C	-	A1	L	I	Q	I	D	
3	:	B	C	C	T	-	A5	F	C	C	-	A1
4	:	B	C	C	T	-	A5	F	C	C	-	A1
5	:	B	C	C	T	-	A5	L	I	Q	I	D
6	:	B	C	C	T	-	A5	L	I	Q	I	D
7	:	F	C	C	-	A1	L	I	Q	I	D	
8	:	F	C	C	-	A1	L	I	Q	I	D	

Sn10wt%Pb



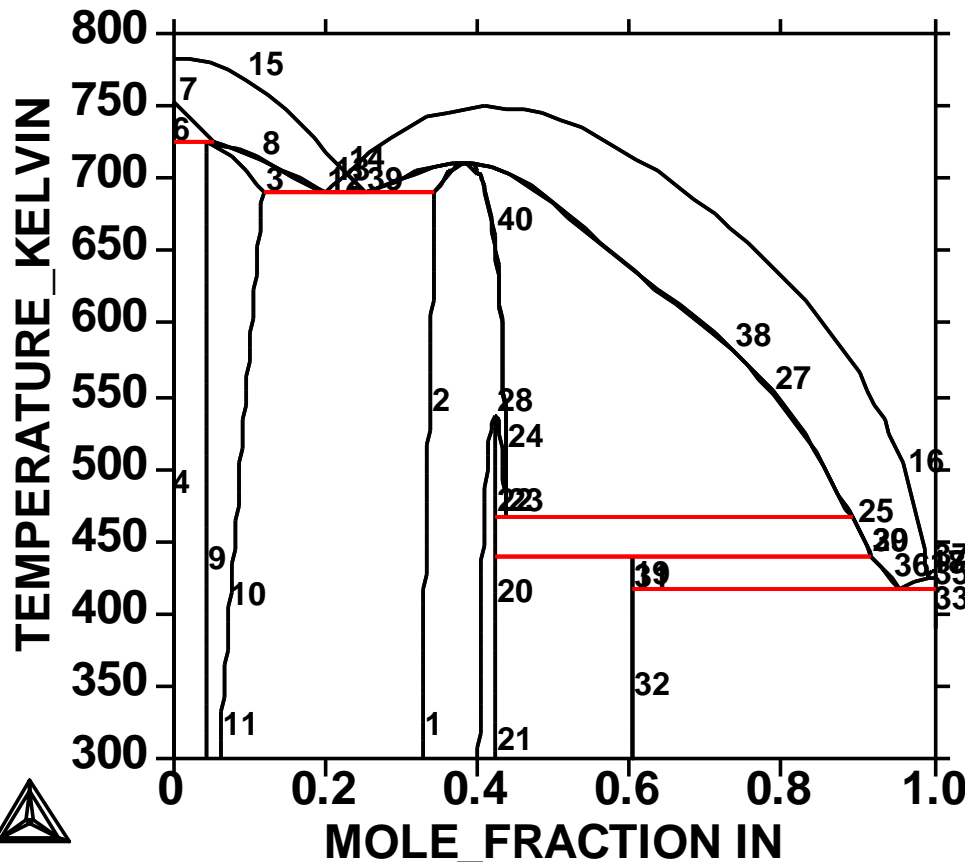
Příklady výstupů metody CALPHAD

DATABASE: SOLDER

N=1, P=100000, X(AG)-X(SB)=-5.55111512E-17;

Database
SOLDER

ThermoCalc

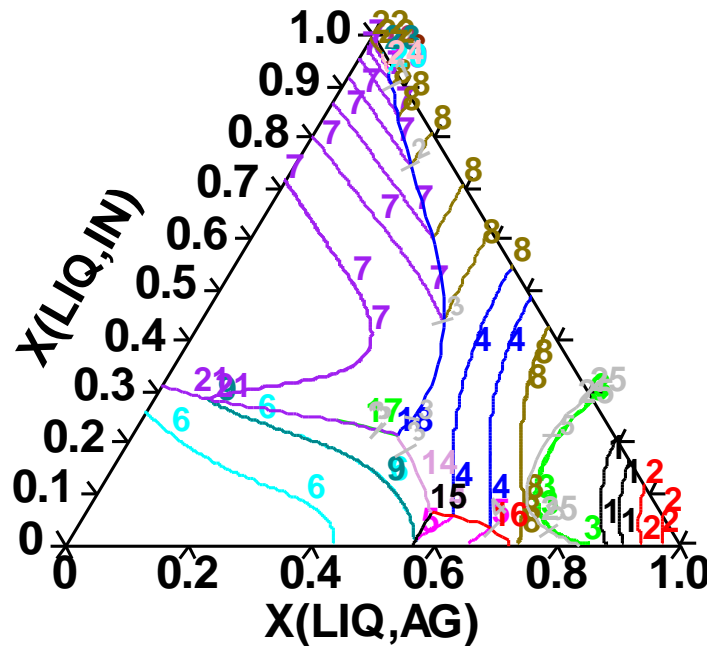


- 1:* RHOMBOHEDRAL_A7 HCP_A3 ZINCBLLENDE_B3
- 2:* RHOMBOHEDRAL_A7 LIQUID ZINCBLLENDE_B3
- 3:* LIQUID HCP_A3
- 4:* HCP_A3 AG2IN ZINCBLLENDE_B3
- 6:* LIQUID AG2IN ZINCBLLENDE_B3
- 7:* AG2IN HCP_A3 ZINCBLLENDE_B3
- 8:* HCP_A3 LIQUID ZINCBLLENDE_B3
- 9:* AG2IN LIQUID ZINCBLLENDE_B3
- 10:* ZINCBLLENDE_B3 LIQUID ZINCBLLENDE_B3
- 11:* ZINCBLLENDE_B3 LIQUID ZINCBLLENDE_B3
- 12:* HCP_A3 LIQUID ZINCBLLENDE_B3
- 13:* ZINCBLLENDE_B3 LIQUID RHOMBOHEDRAL_A7
- 14:* RHOMBOHEDRAL_A7 LIQUID ZINCBLLENDE_B3
- 15:* RHOMBOHEDRAL_A7 LIQUID ZINCBLLENDE_B3
- 16:* ZINCBLLENDE_B3 LIQUID ZINCBLLENDE_B3
- 17:* ZINCBLLENDE_B3 LIQUID TETRAGONAL_A6
- 18:* TETRAGONAL_A6 LIQUID ZINCBLLENDE_B3
- 19:* LIQUID AG2IN ZINCBLLENDE_B3
- 20:* AG2IN AG2IN ZINCBLLENDE_B3
- 21:* AG2IN AG2IN ZINCBLLENDE_B3
- 22:* LIQUID AG2IN ZINCBLLENDE_B3
- 23:* AG2IN HCP_A3 ZINCBLLENDE_B3
- 24:* LIQUID HCP_A3 ZINCBLLENDE_B3
- 25:* AG2IN LIQUID ZINCBLLENDE_B3
- 27:* HCP_A3 LIQUID ZINCBLLENDE_B3
- 28:* HCP_A3 AG2IN ZINCBLLENDE_B3
- 29:* AG2IN LIQUID ZINCBLLENDE_B3
- 30:* AG2IN LIQUID ZINCBLLENDE_B3
- 31:* AG2IN AG2IN ZINCBLLENDE_B3
- 32:* TETRAGONAL_A6 AG2IN ZINCBLLENDE_B3
- 33:* AG2IN TETRAGONAL_A6 ZINCBLLENDE_B3
- 35:* LIQUID TETRAGONAL_A6 ZINCBLLENDE_B3
- 36:* AG2IN LIQUID ZINCBLLENDE_B3
- 37:* TETRAGONAL_A6 LIQUID
- 38:* HCP_A3 LIQUID ZINCBLLENDE_B3
- 39:* RHOMBOHEDRAL_A7 LIQUID ZINCBLLENDE_B3

Plocha liquidu

Bod tání dle termické analýzy

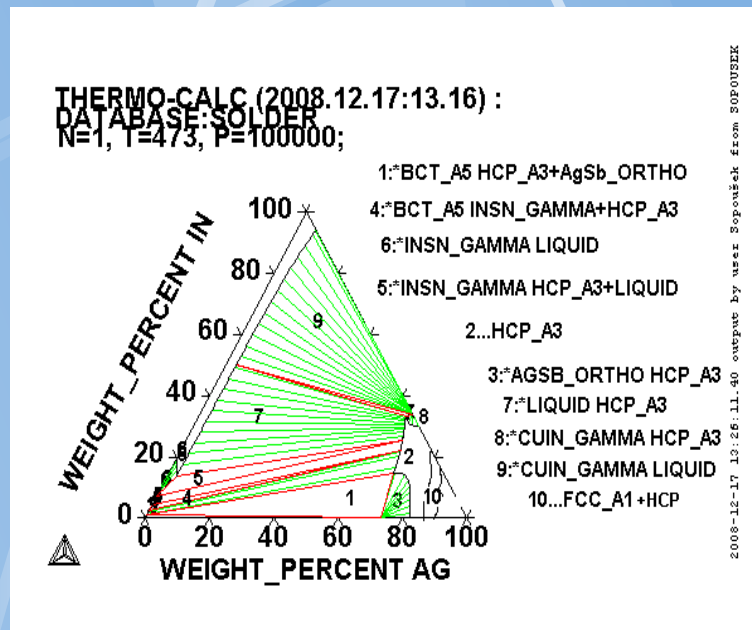
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 DATABASE:SOLDER
 Z-AXIS = 400.0 + 100.0 * Z



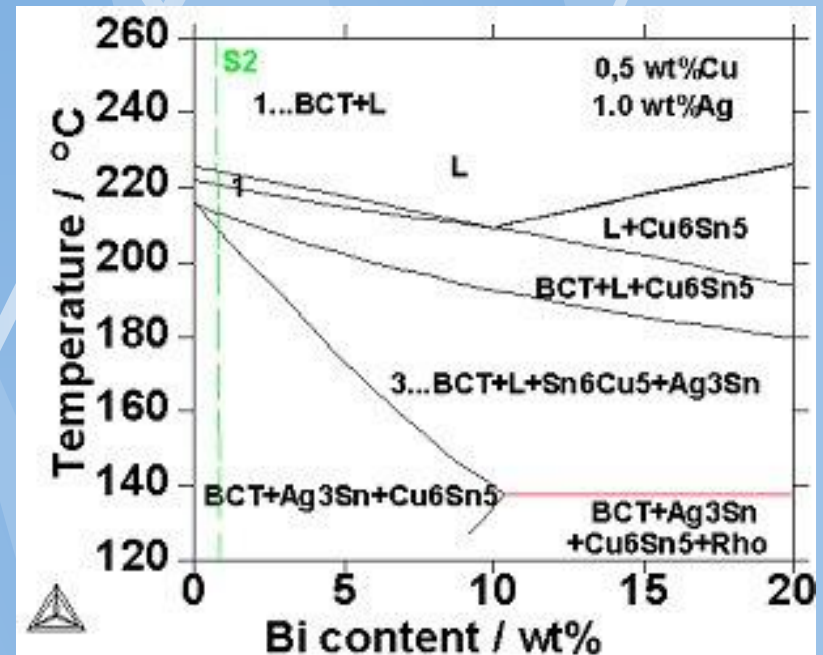
1:* LIQUID FCC_A1
 2:* FCC_A1 LIQUID
 3:* FCC_A1 HCP_A3
 4:* LIQUID HCP_A3
 5:* AGSB_ORTHO LIQUID
 6:* RHOMBOHEDRAL_A7 LIQUID
 7:* ZINCBLLENDE_B3 LIQUID
 8:* HCP_A3 LIQUID
 9:* LIQUID RHOMBOHEDRAL_A7
 10:* AG2IN ZINCBLLENDE_B3
 11:* AG2IN TETRAGONAL_A6
 12:* ZINCBLLENDE_B3 TETRAGONAL_A6
 13:* AG2IN LIQUID
 14:* LIQUID HCP_A3 F0 RHOMBOHEDRAL_A7
 15:* AGSB_ORTHO F0 LIQUID RHOMBOHEDRAL_A7
 16:* AGSB_ORTHO HCP_A3 F0 LIQUID
 17:* LIQUID F0 RHOMBOHEDRAL_A7
 18:* LIQUID HCP_A3 F0 ZINCBLLENDE_B3
 19:* AG2IN F0 LIQUID ZINCBLLENDE_B3
 20:* AG2IN HCP_A3 F0 LIQUID
 21:* RHOMBOHEDRAL_A7 LIQUID F0
 22:* TETRAGONAL_A6 LIQUID F0
 23:* AG2IN LIQUID F0 TETRAGONAL_A6
 24:* AG2IN LIQUID F0 ZINCBLLENDE_B3
 25:* HCP_A3 FCC_A1 F0 LIQUID

2004.06.16:10.35 output by user Sopoušek fr

Aplikace metody – fázové diagramy



Predikovaný isotermní řez
 fázovým diagramem soustavy
 Sn-Ag-In pro 200°C.



Predikovaný isokoncentrační řez fázovým
 diagramem soustavy Sn-1%Ag-0,5%Cu-
 Bi. Zelená přerušovaná čára vyznačuje
 složení sledované slitiny Sn-3,5%Ag-
 0,7%Cu-1%Bi.

CALPHAD – výpočet FD

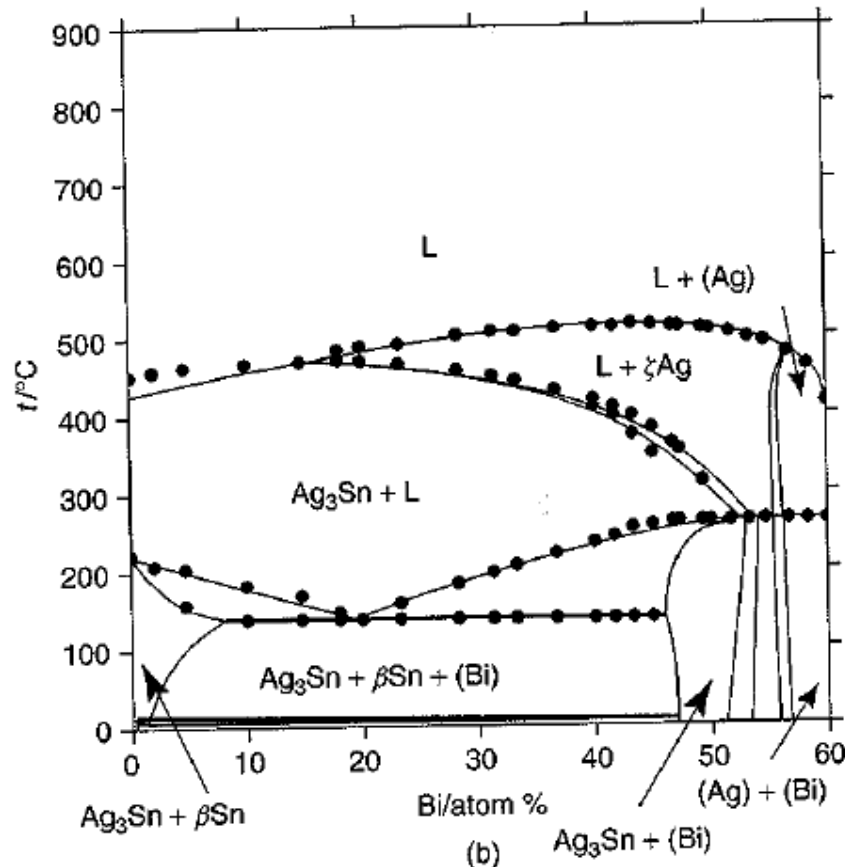


Figure 1 Comparison of the calculated vertical section diagrams of the Sn-Ag-Bi system with the DSC data at: (a) 10 mol% Bi; and (b) 40 mol% Ag

Včetně exp.
Měření DSC

FD Sn-Bi-Ag pájek

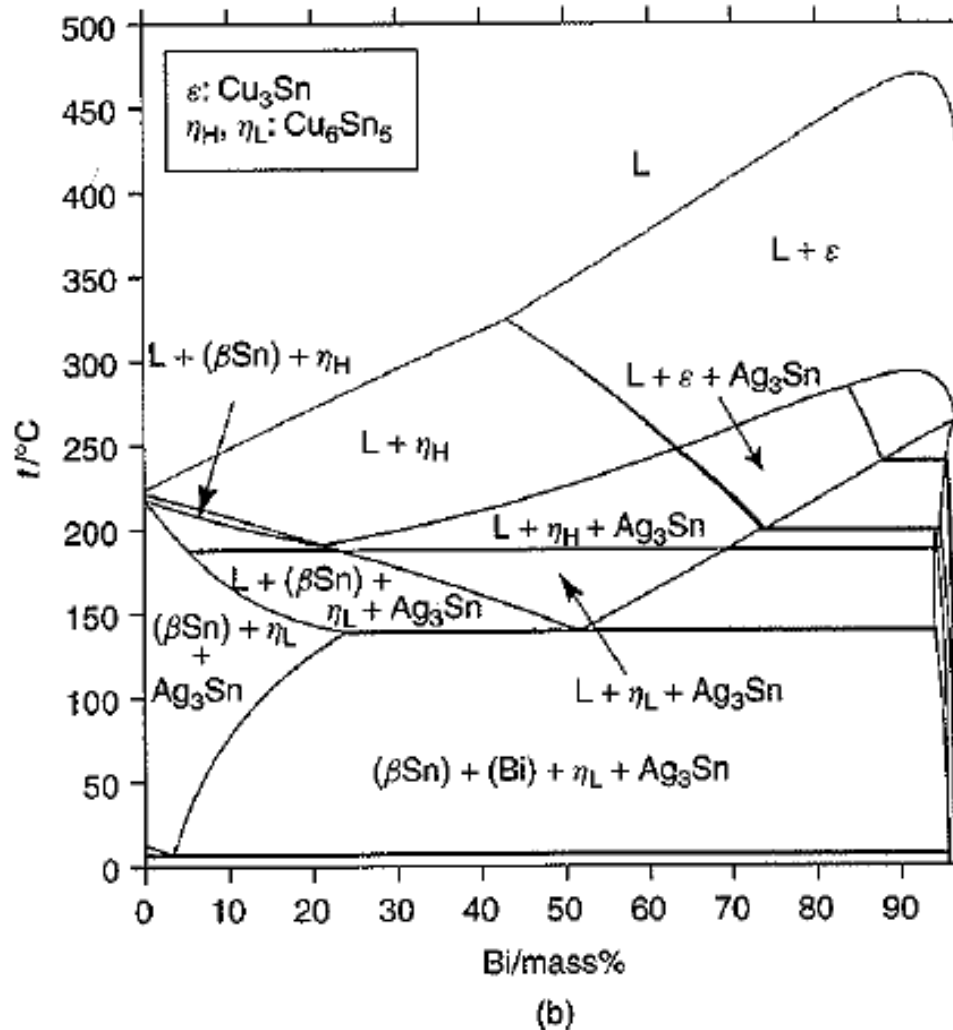
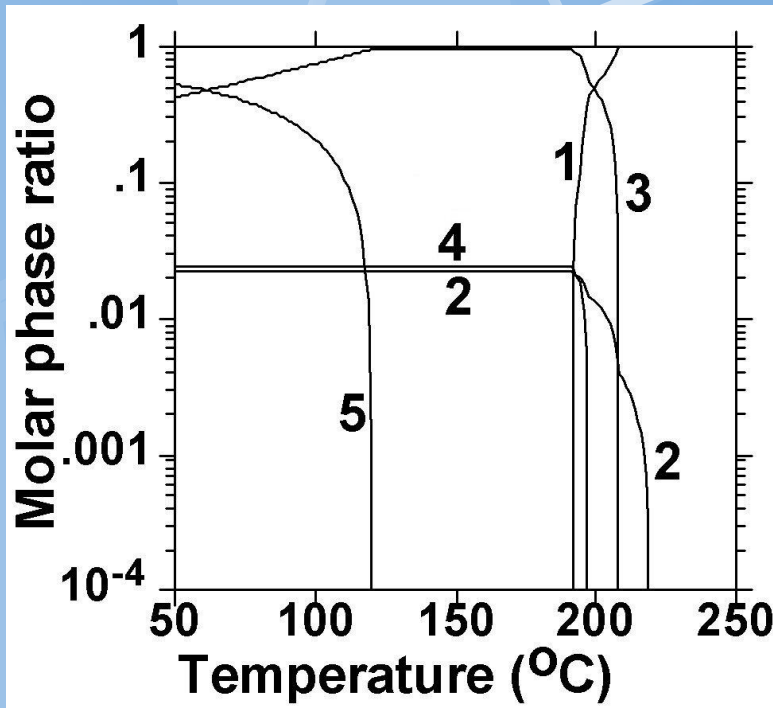
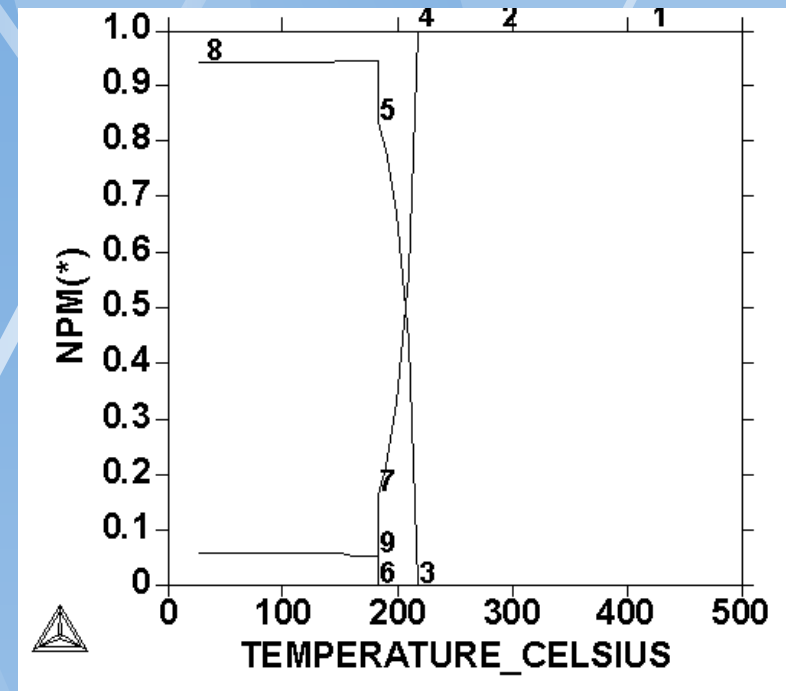


Figure 2 Comparison of the vertical section diagrams of: (a) Sn-Bi-2mass%Ag; and (b) Sn-Bi-2mass% Ag-0.7 mass% Cu alloys

Teplotní stabilita fází



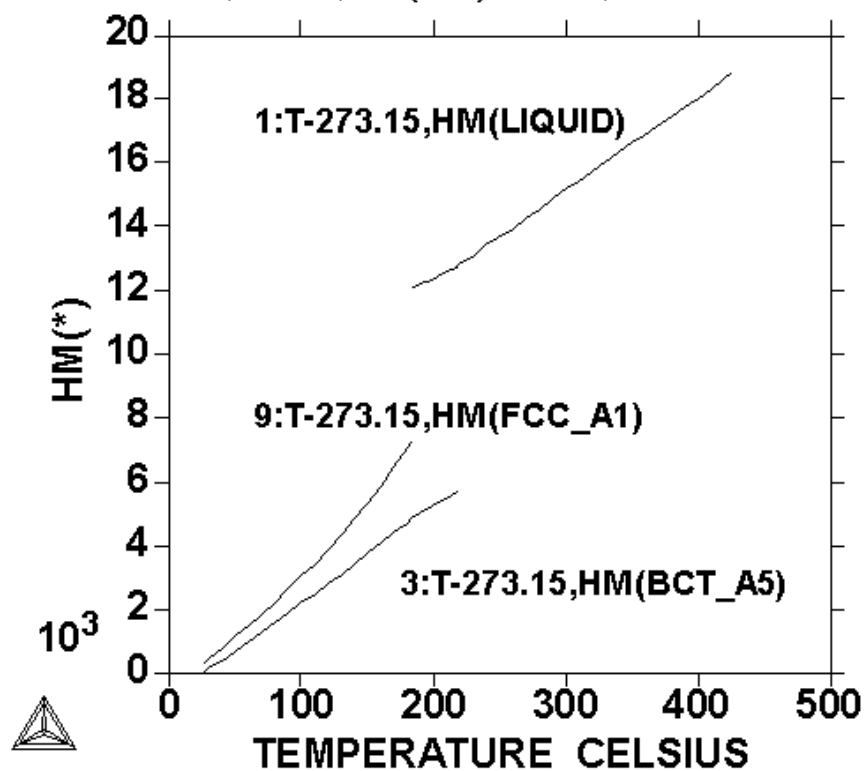
Závislost rovnovážného molárního podílu fází na teplotě pro soustavu Sn-3,5wt%Ag-0,7%Cu (1-liquid, 2- Cu_3Sn_6 , 3- Ag_3Sn). Bod tání 217°C .



Závislost rovnovážného molárního podílu fází na teplotě pro soustavu Sn-10wt%Pb (1-liquid, 5-BCT_A5, 7-FCC_A1). Bod liquidu 218°C , solisu 182°C .

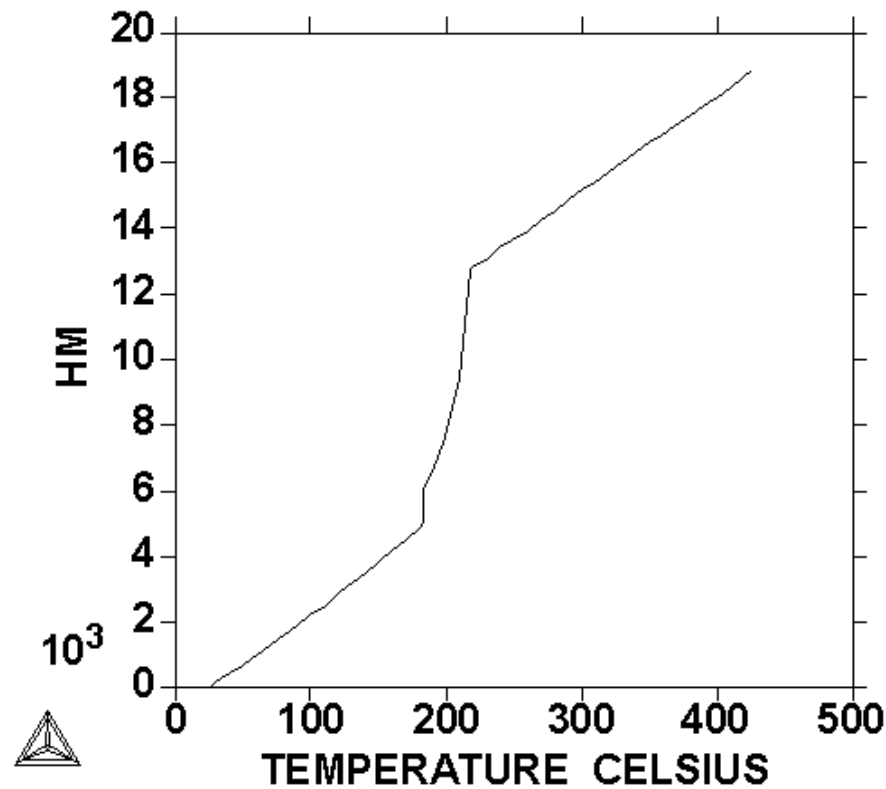
Entalpie slitiny 10Wt%Pb-Sn

THERMO-CALC (2012.05.31:13.28) :
DATABASE: SOLDER
P=100000, N=1., W(PB)=1E-1;



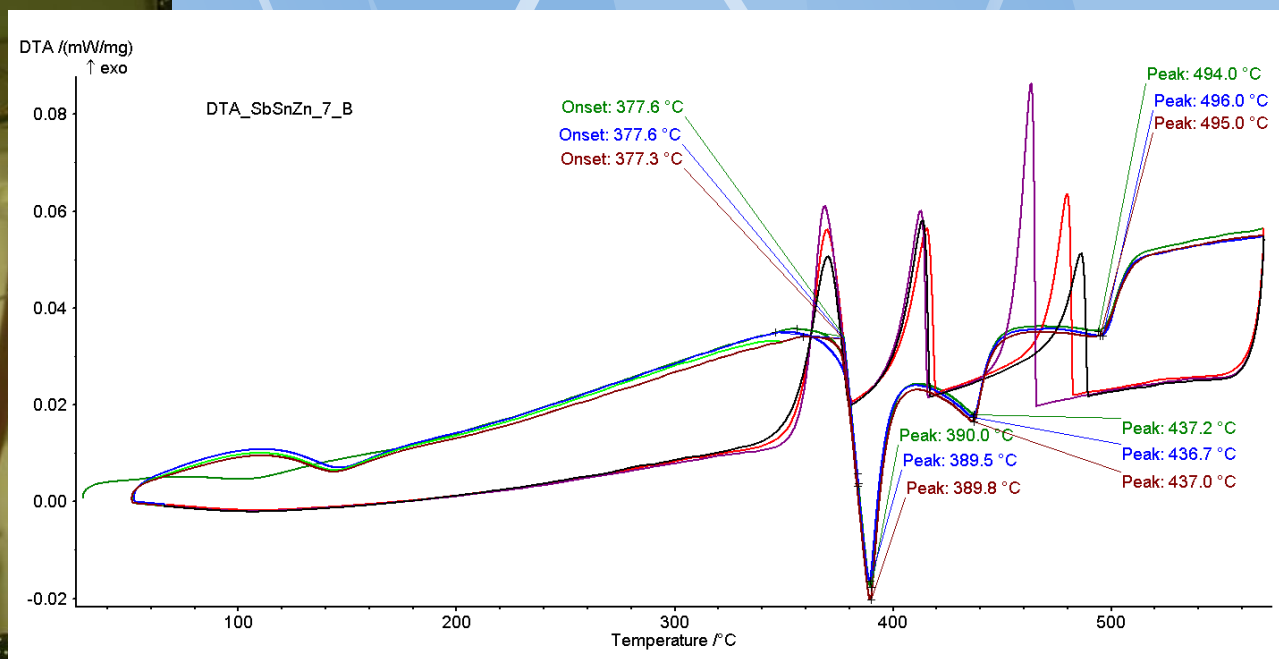
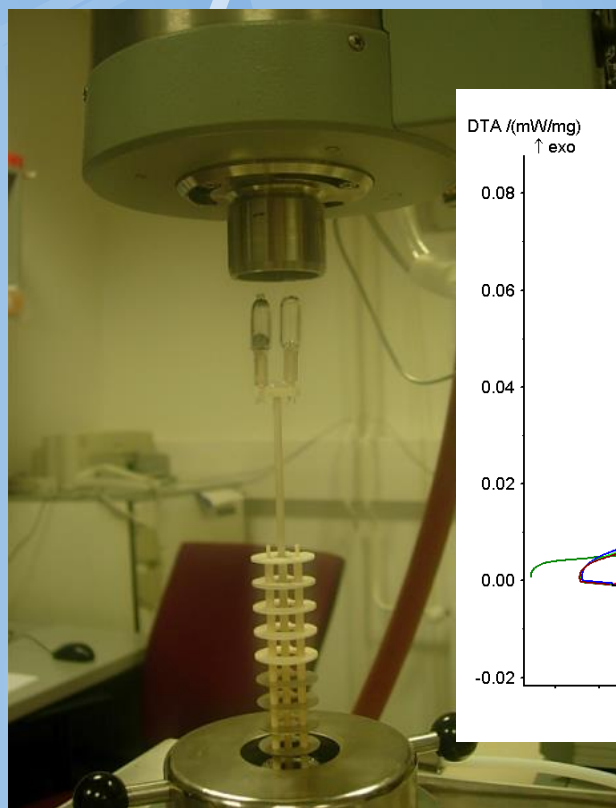
Entalpie koexistujících fází.

DATABASE: SOLDER
P=100000, N=1., W(PB)=1E-1;



Entalpie celková.

Simulace signálů DTA, pcDSC a hfDSC



Dobře reprodukovatelné měření

Signál DTA (hfDSC)

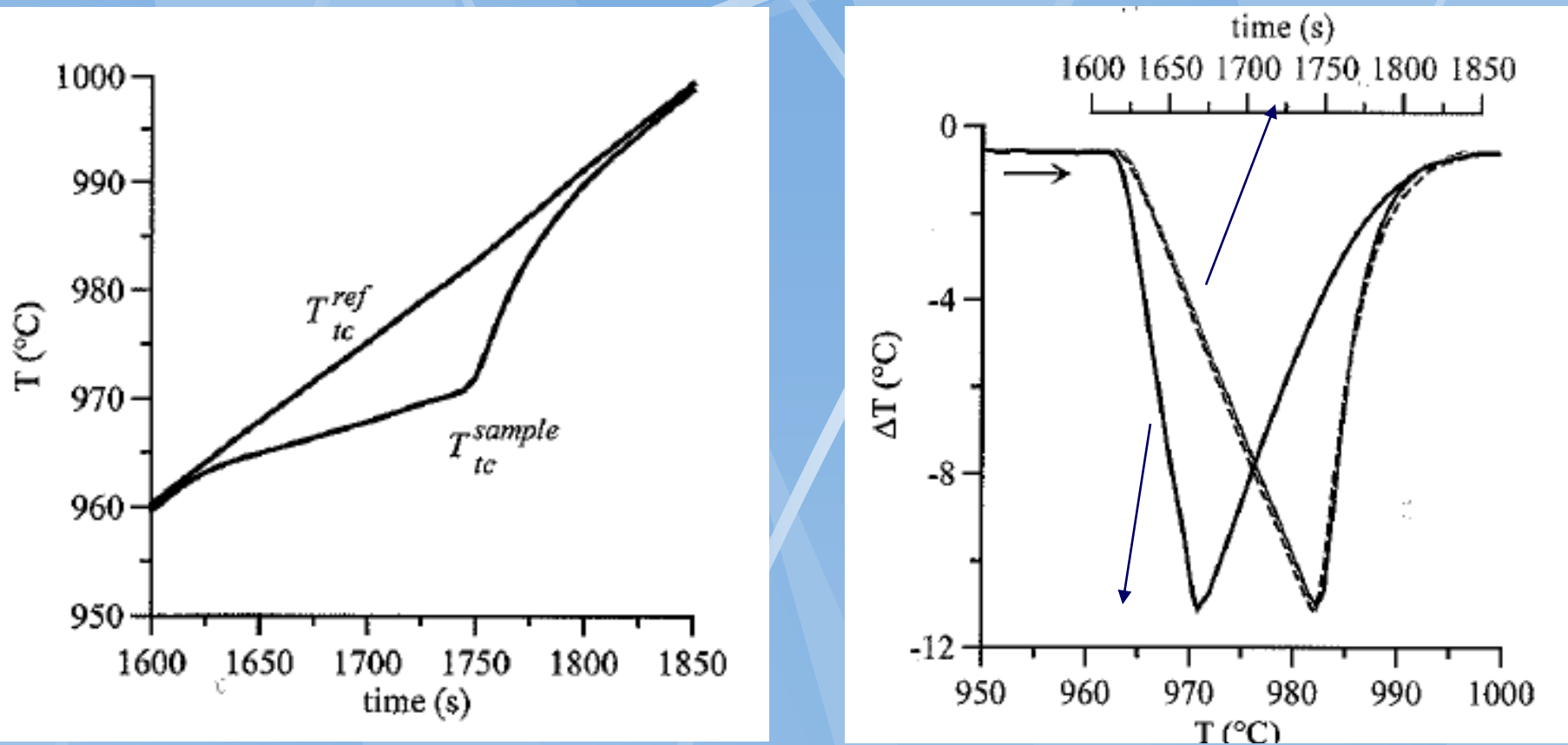


Figure 2.2. DTA melting of a 211.6 mg of pure Ag at 10 K/min. (a) Reference thermocouple temperature T_{tc}^{ref} and sample thermocouple temperature T_{tc}^{sample} vs. time. (b) Differential signal $\Delta T = T_{tc}^{sample} - T_{tc}^{ref}$ vs. time (red), vs. sample temperature (solid black), and vs. reference temperature (dashed black). For this data, the reference temperature remains quite linear in time as the sample melts, so that a linear scaling of the time axis makes the plots with x-axes of time and reference temperature practically identical.

Zpoždění reálného signálu

Přestup tepla (šikmost) v.s. přímé vložení termočlánku (kolmé)

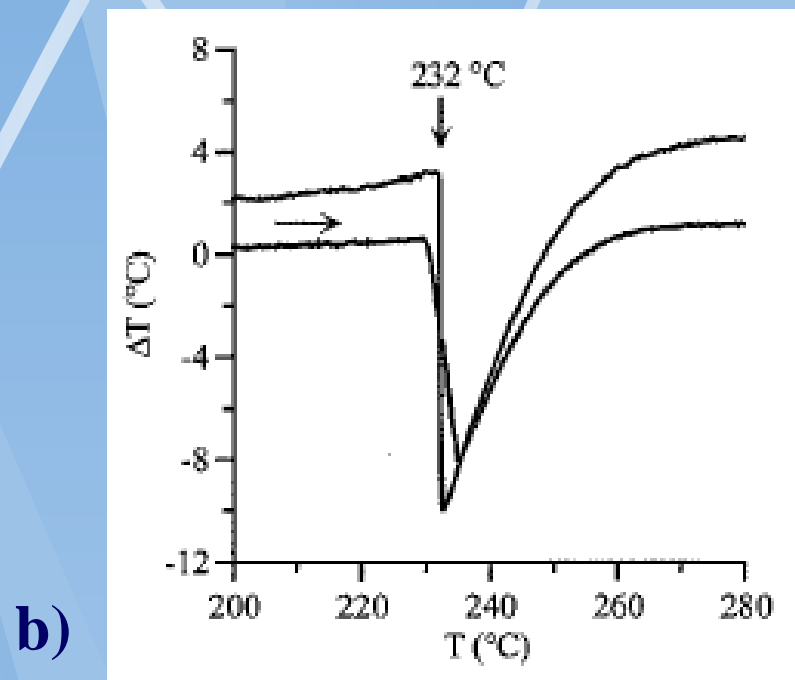
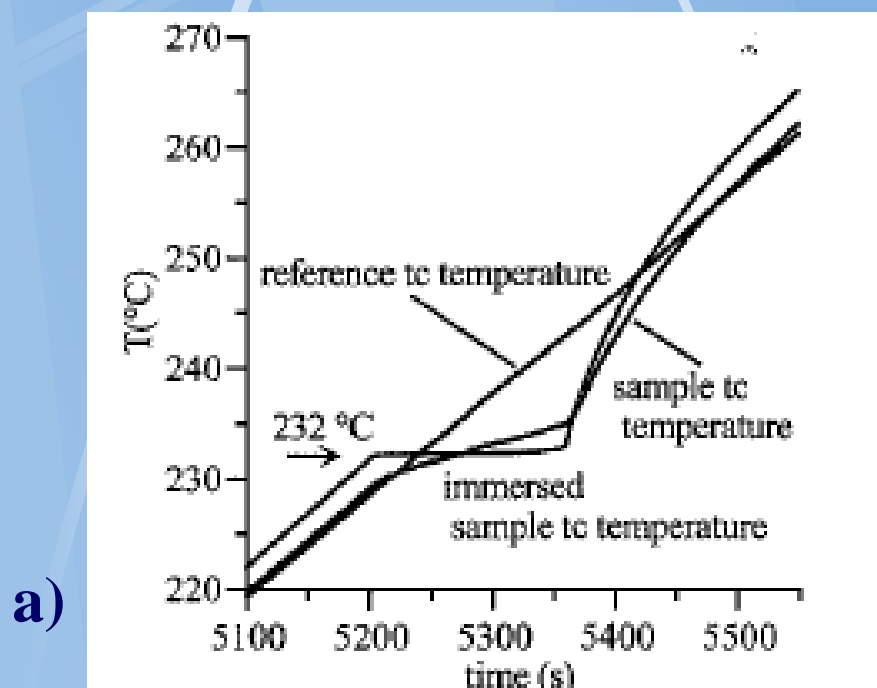


Figure 2.6. Measured (a) temperature vs. time plots and (b) associated DTA plots for melting of pure Sn. The instrument thermocouple readings are black and the readings from a thermocouple immersed directly in the Sn in the sample cup is red. Mass = 163.2 mg; heating rate = 5 K/min.

Efekt podchlacení na křivce chladnutí čistého Sn

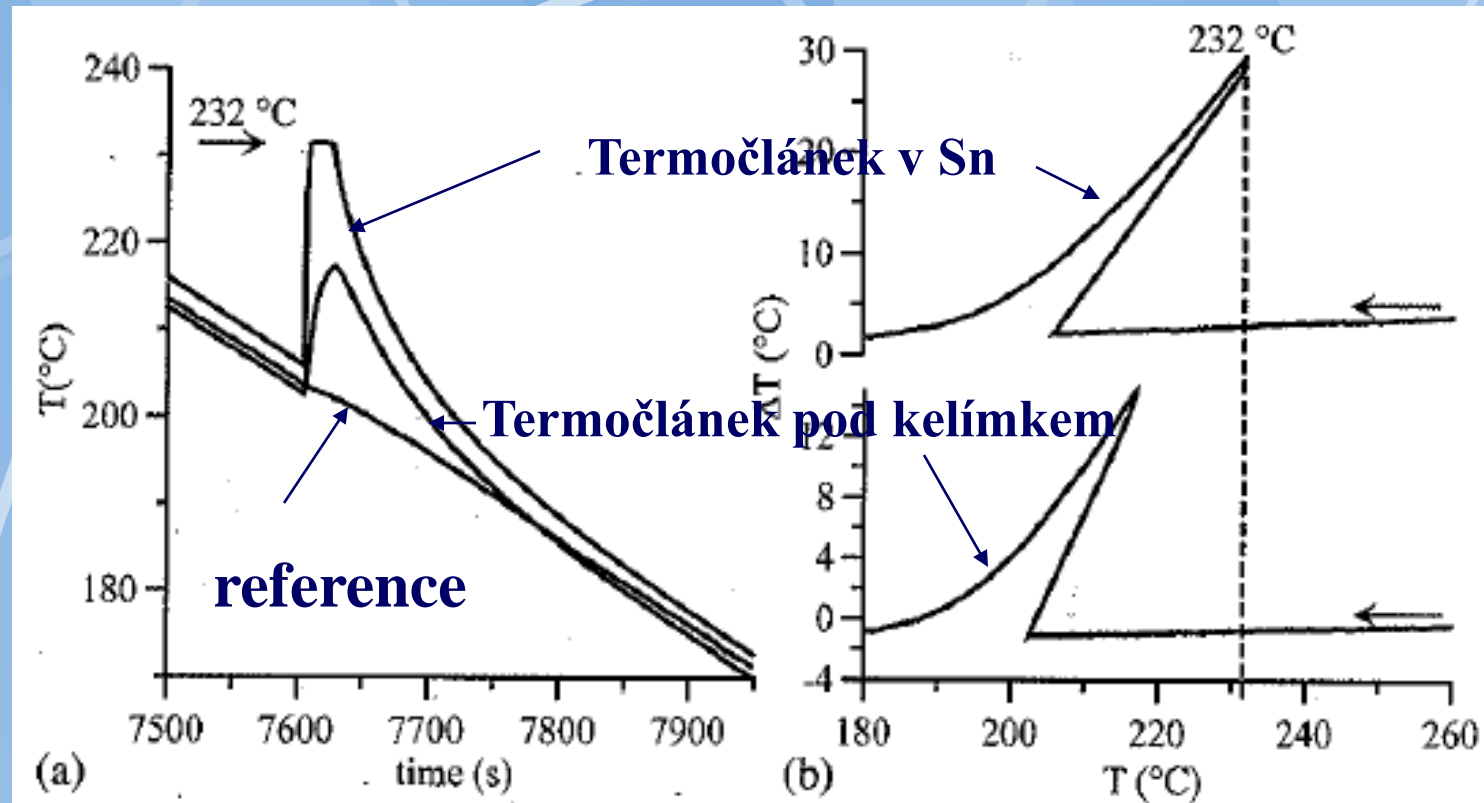
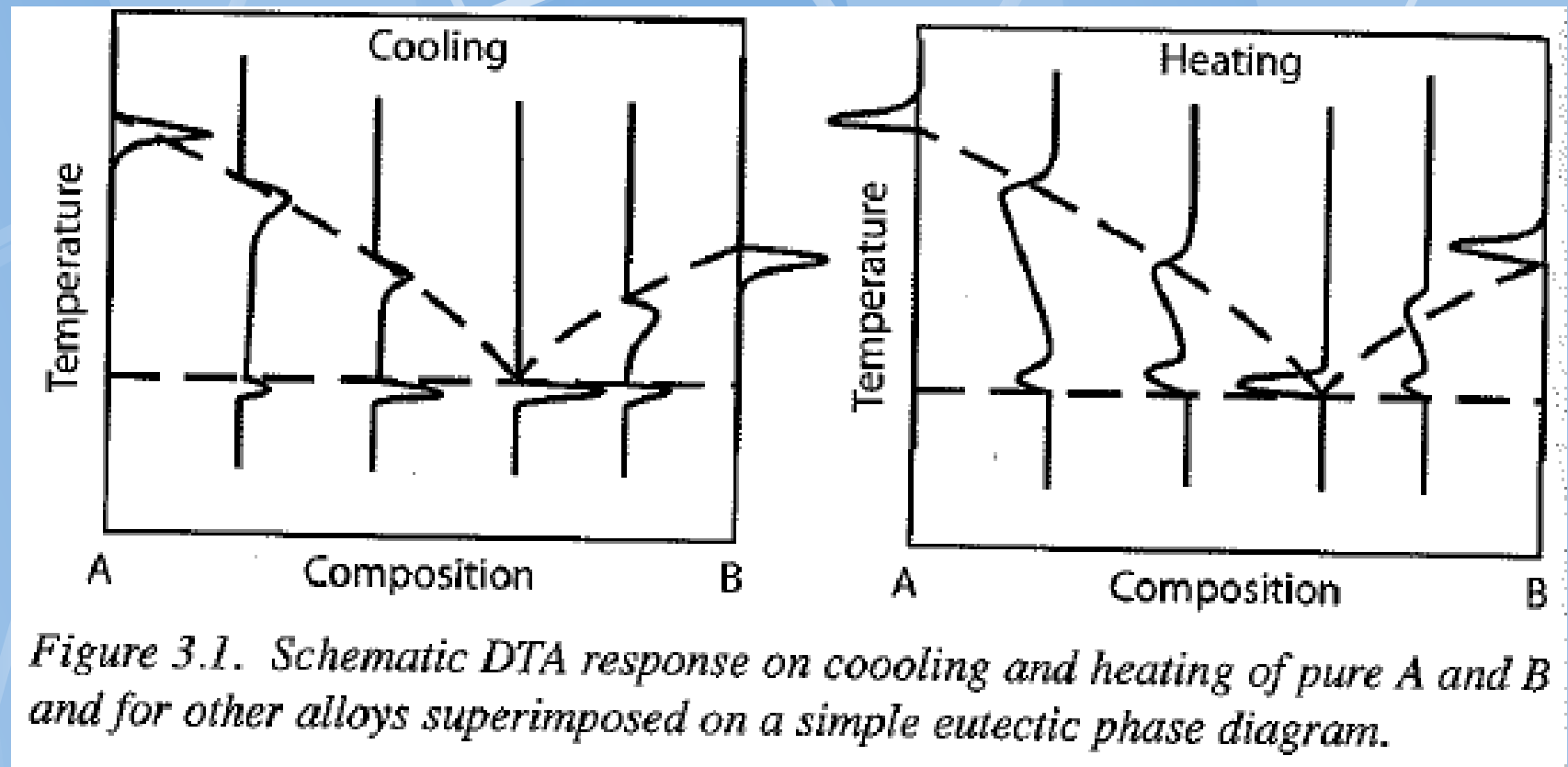


Figure 3.15. Measured (a) temperature vs. time plots and (b) associated DTA plots for the freezing of pure Sn. The instrument thermocouple readings (sample and reference) are black and the readings from a thermocouple immersed directly into the Sn in the sample cup are red. Significant supercooling has occurred prior to freezing inducing the rapid temperature rise upon solidification in (a) and the associated positive slope in (b); mass = 163.2 mg; heating rate = 5 K/min.

DTA binárních slitin Klasické výhodnocení



**Aplikovatelné jen pro
jednoduché případy**

Princip simulace DTA (DSC)

Figure 2.5. Schematic a) enthalpy vs. temperature for a pure metal; b) corresponding derivative $dH_S(T_S)/dT_S$ curve; c) DTA signal for melting (bottom) and freezing (top). The small difference in heat capacity of liquid and solid leads to a small offset of the baseline before and after melting. The onsets in the DTA curves are shown with a small deviation from the melting point, T_M , due to heat flow limitation in the DTA. This difference on melting is adjusted to zero by the calibration procedure, at least for one heating rate.

$$dH^m/dt = C_p^m$$

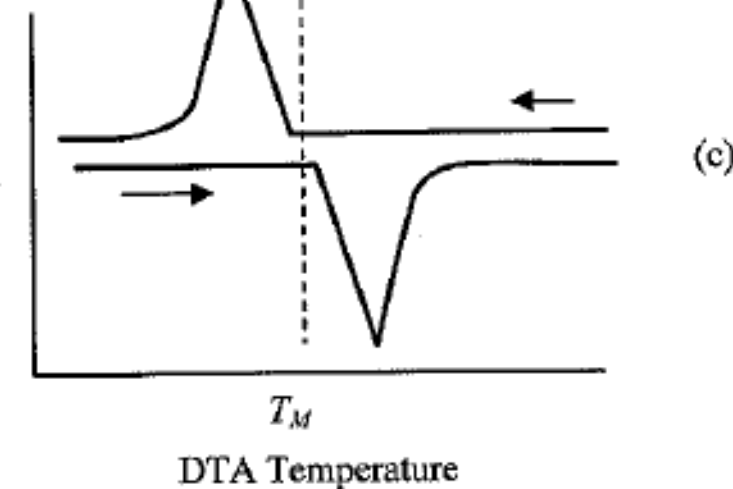
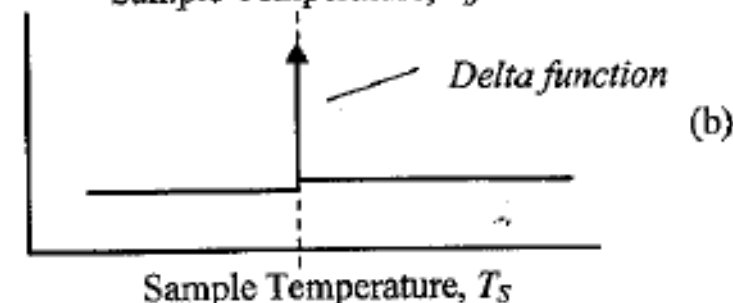
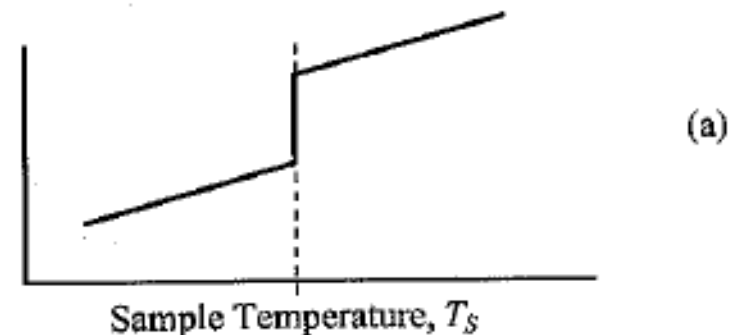
Pro fázovou přeměnu 1.ř:

$dH^m/dt = \text{neko}$
 nečno. (delta
 funkce)

Zpoždění,
podchlazení,
posuv

Sample Enthalpy,
 H_S

dH_S/dT_S



CALPHAD přínos – výpočet entalpie

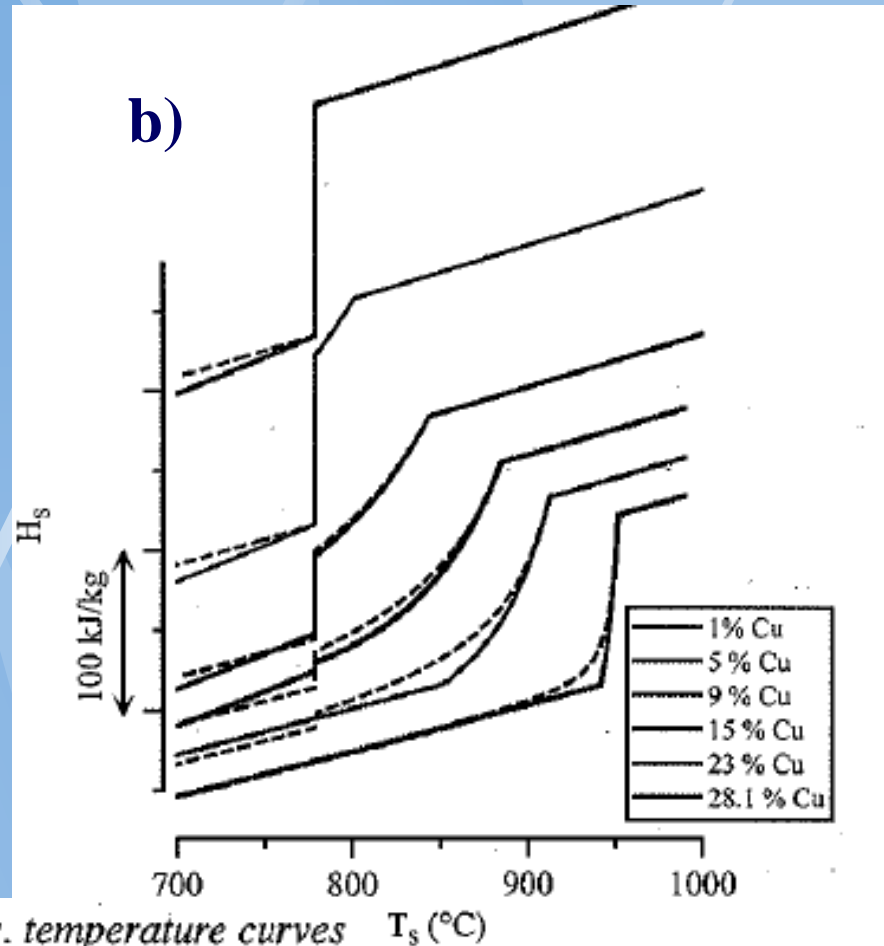
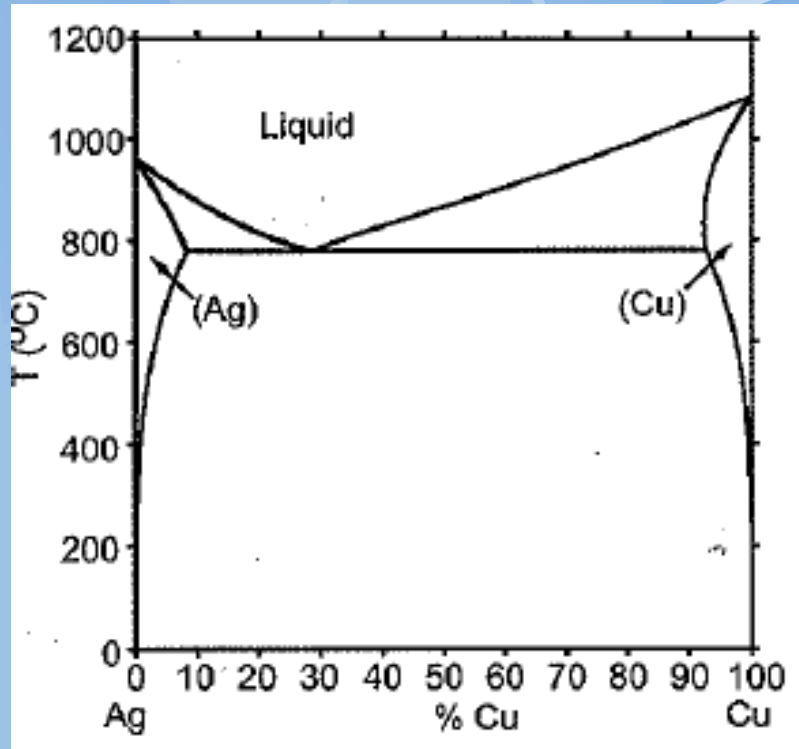
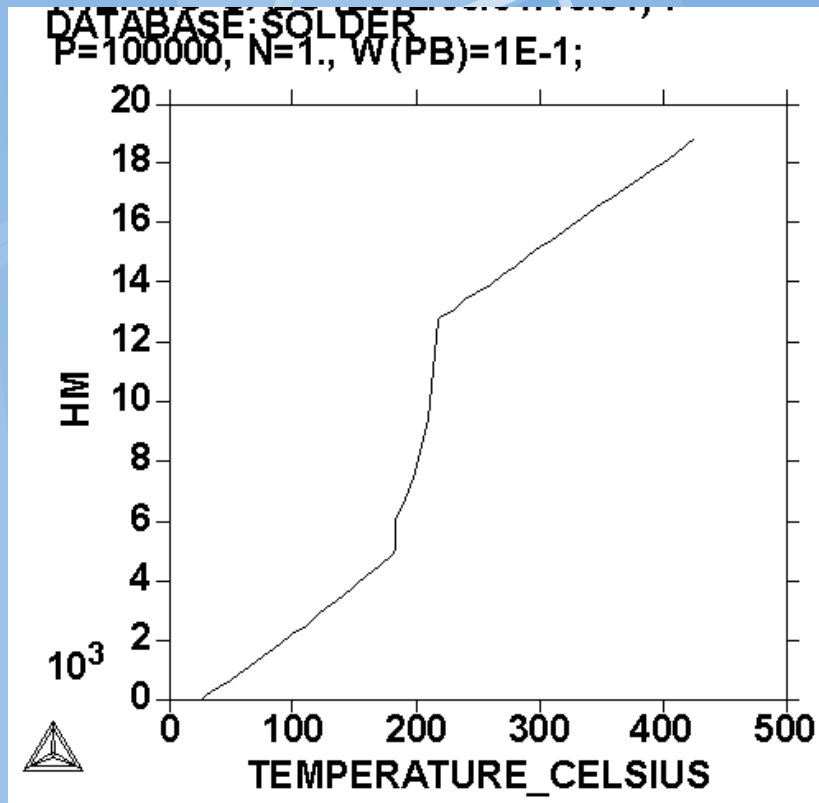
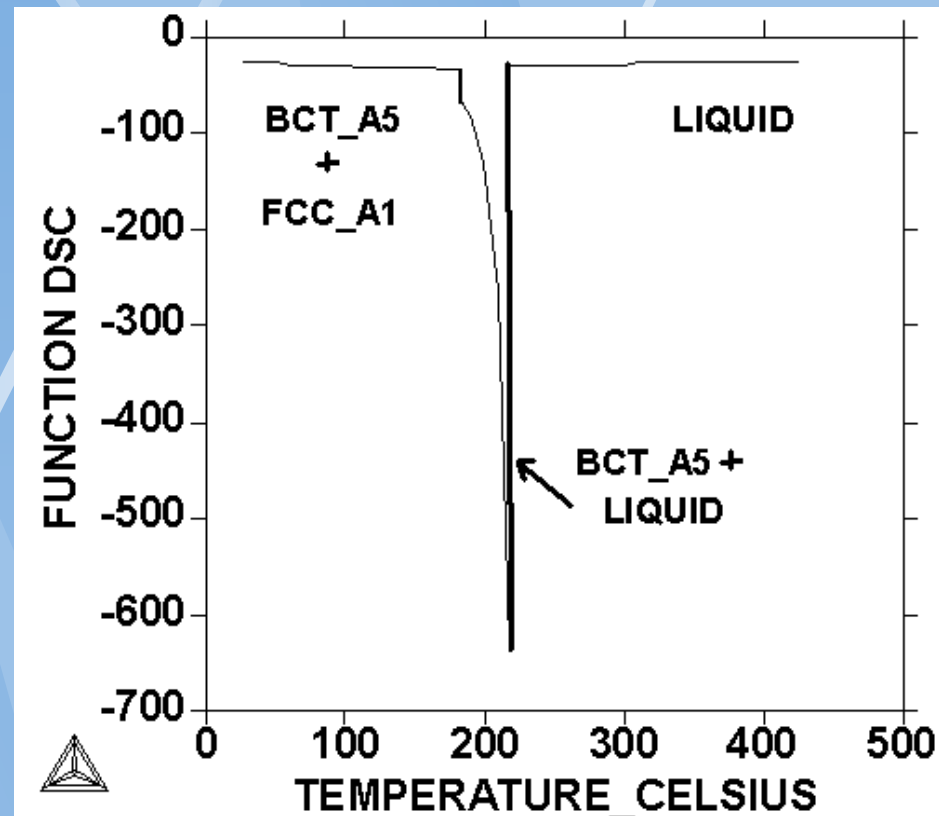


Figure 3.2. (a) Ag-Cu phase diagram; (b) Enthalpy vs. temperature curves for five Ag-Cu alloys (solid, equilibrium; dashed, Scheil); the curves have been shifted vertically for clarity, only differences of enthalpy are relevant; (c) dH_S / dT_S vs. T_S curves for equilibrium conditions for various Ag-Cu alloys derived from the equilibrium enthalpy curves (overleaf). The vertical arrows at the eutectic temperature (779°C) represent delta functions of the indicated strength in kJ/kg.

Sn-10wt%Pb



Entalpie celková.



Funkce DSC= $dH^m/dt=C_p^m$

DSC čisté látky a binární nízkoalegované slitiny

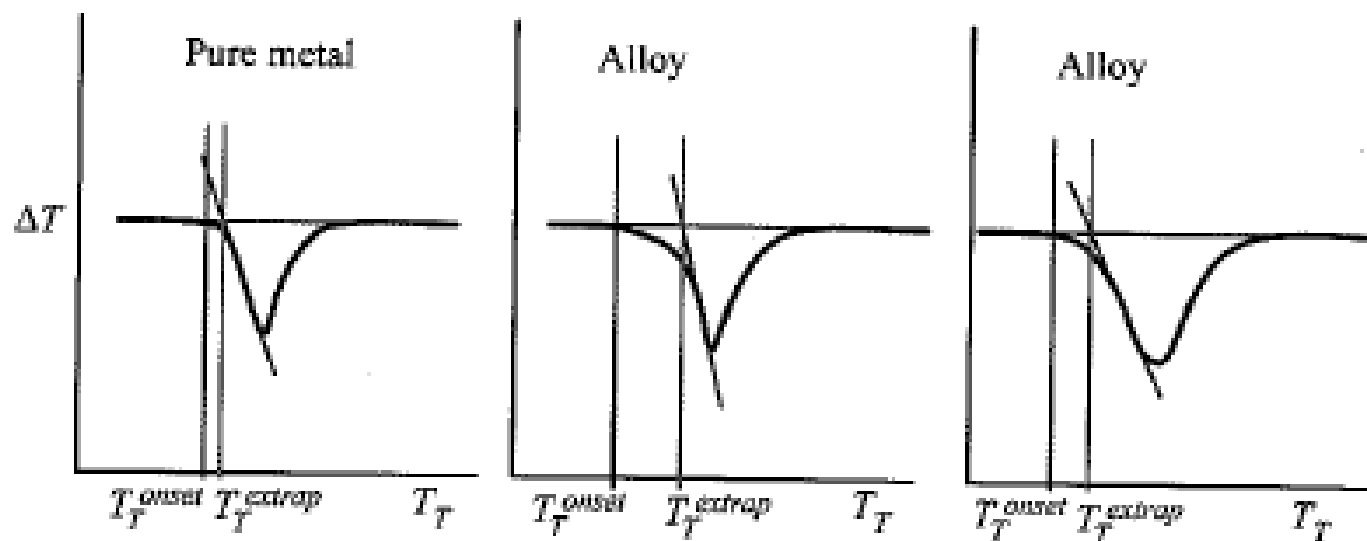
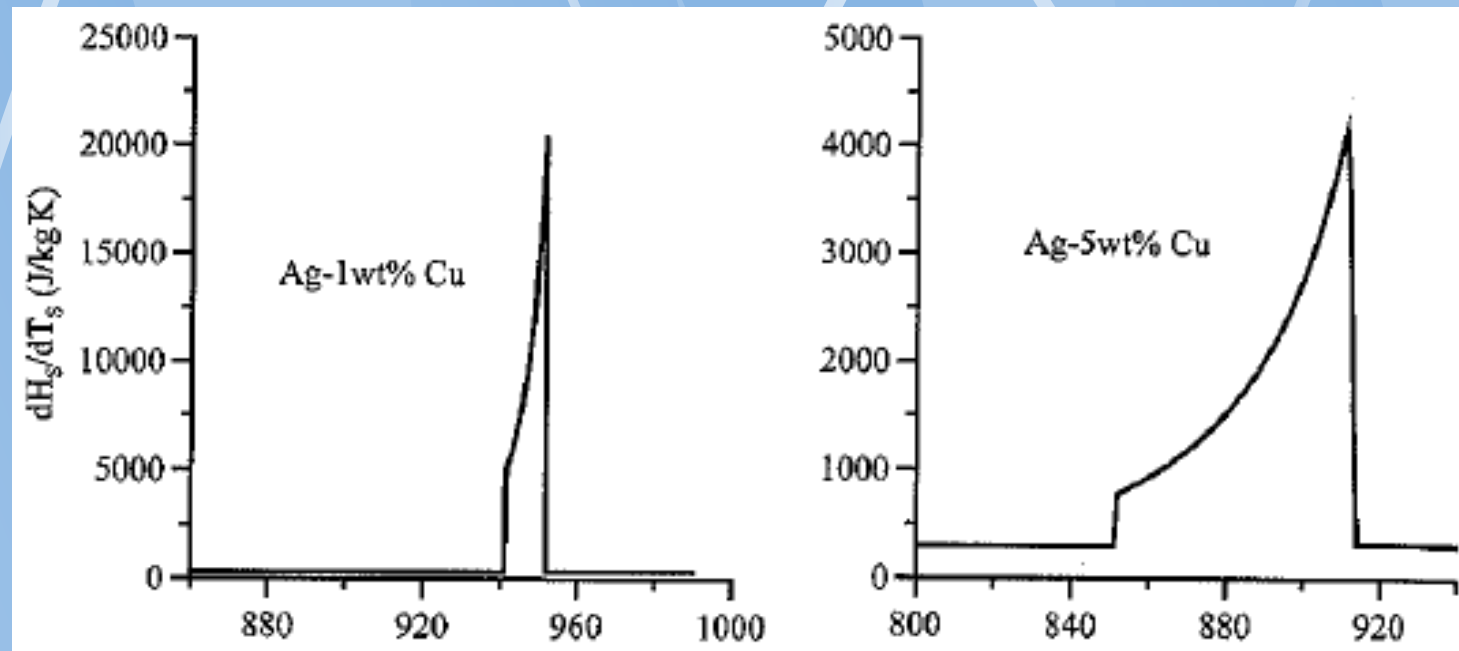
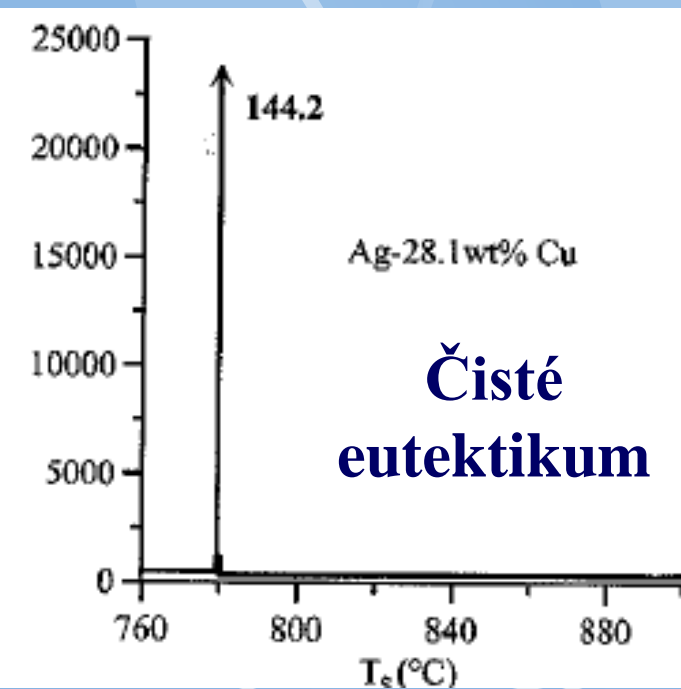
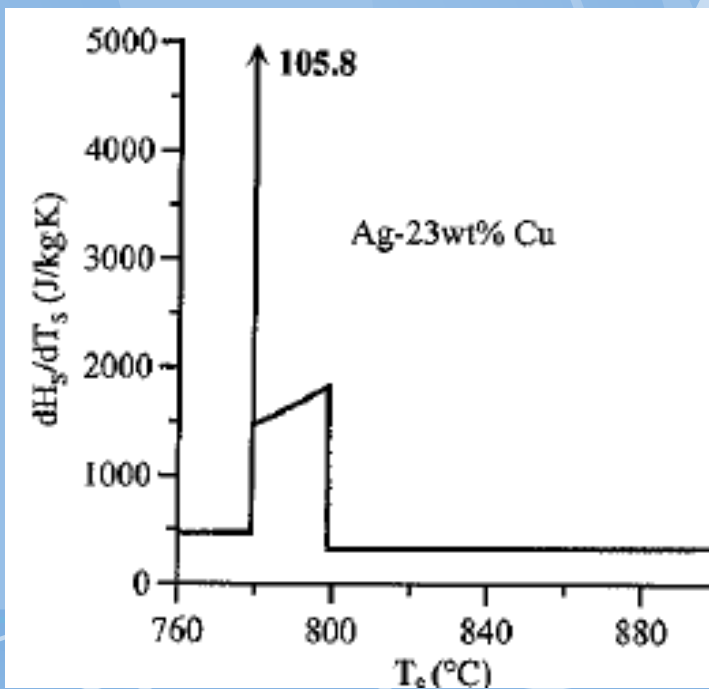
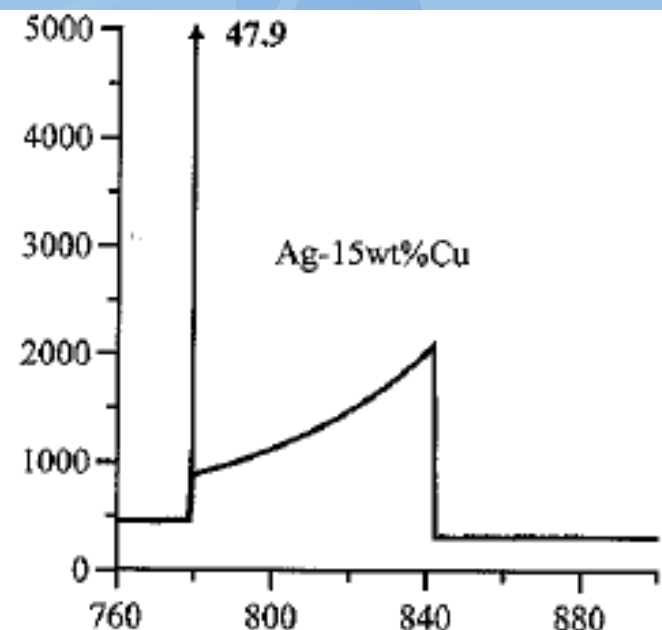
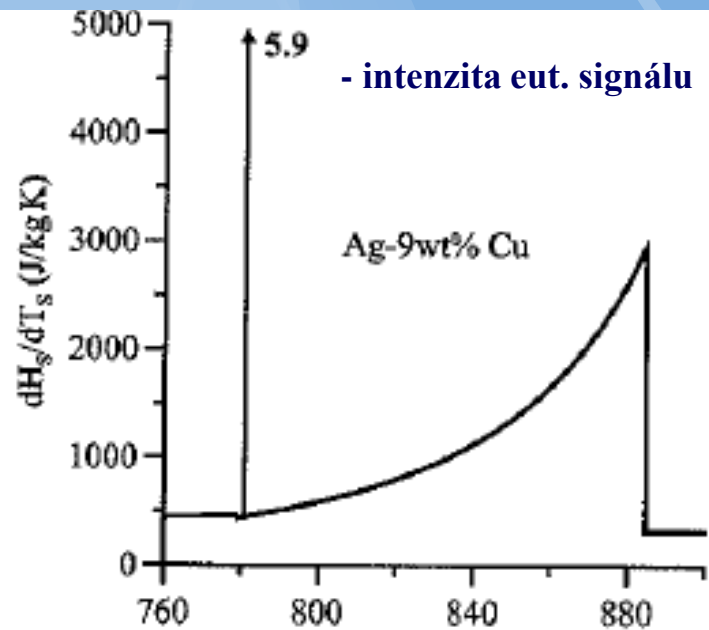


Figure 3.8. Schematic DTA plots showing error introduced by using the extrapolation method for onset determination rather than the first detectable departure from baseline.

**Použití i pro testy čistoty
látek.**

Derivace entalpie bináru SnAg





Reálný DTA (DSC) signál bináru SnAg

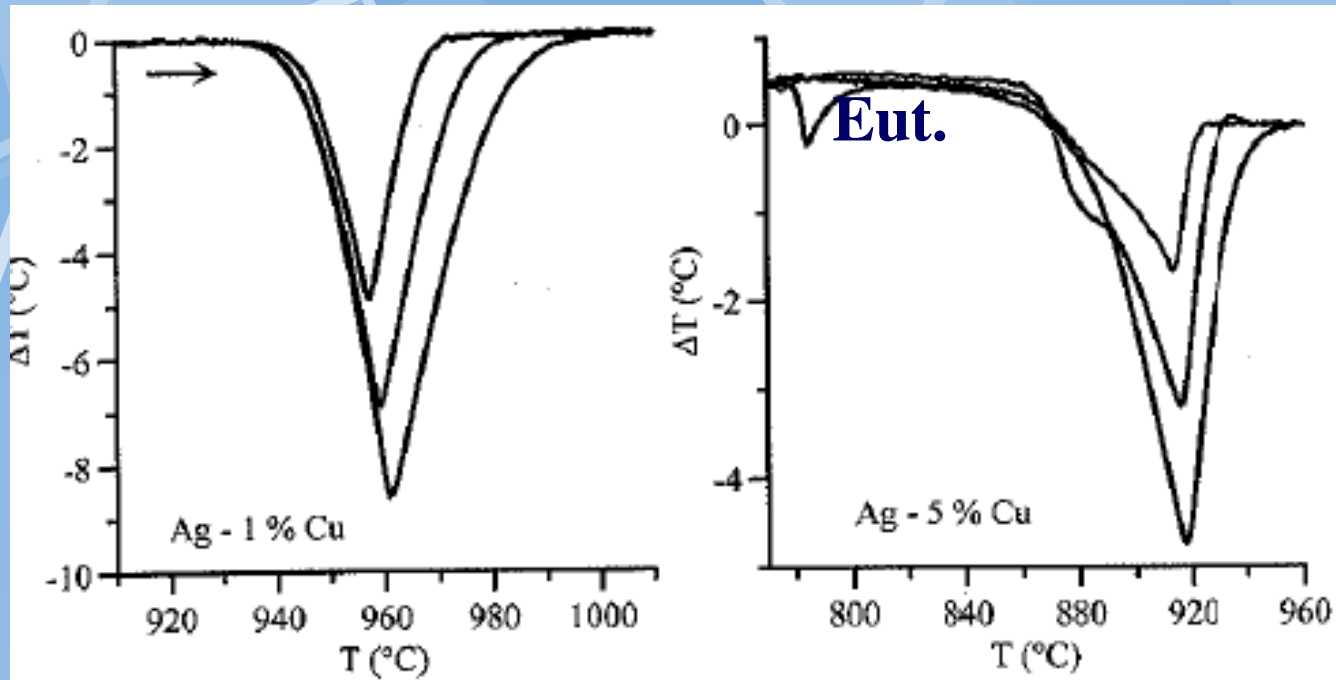
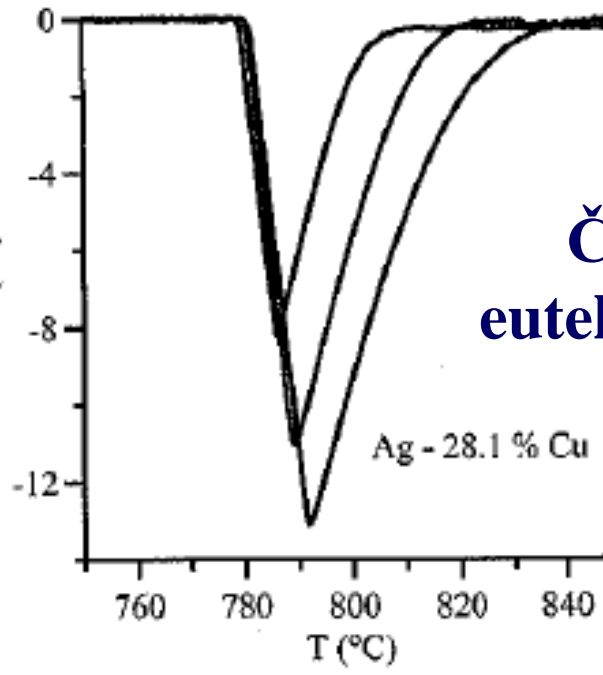
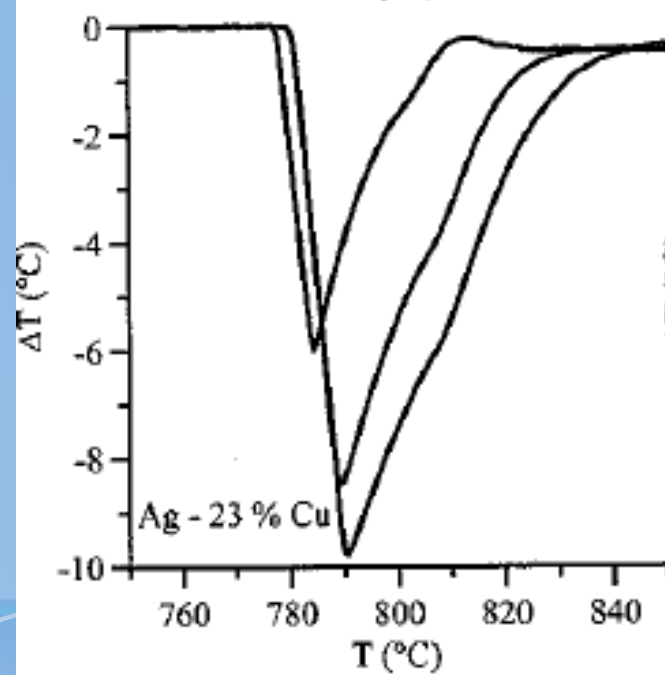
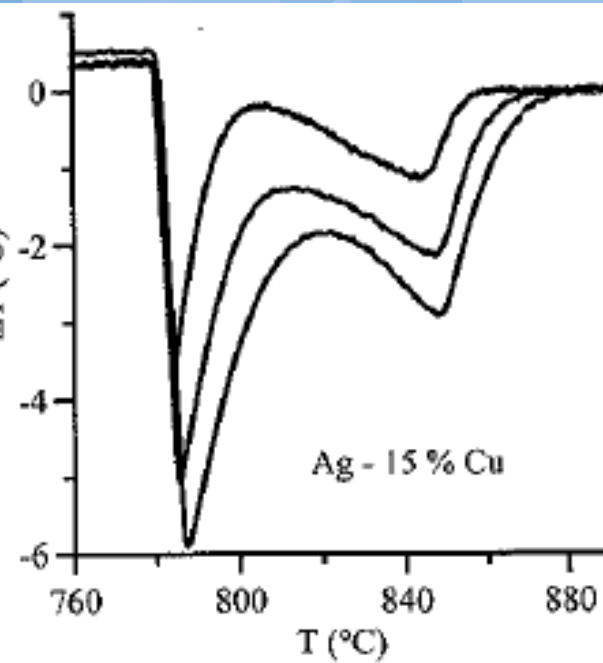
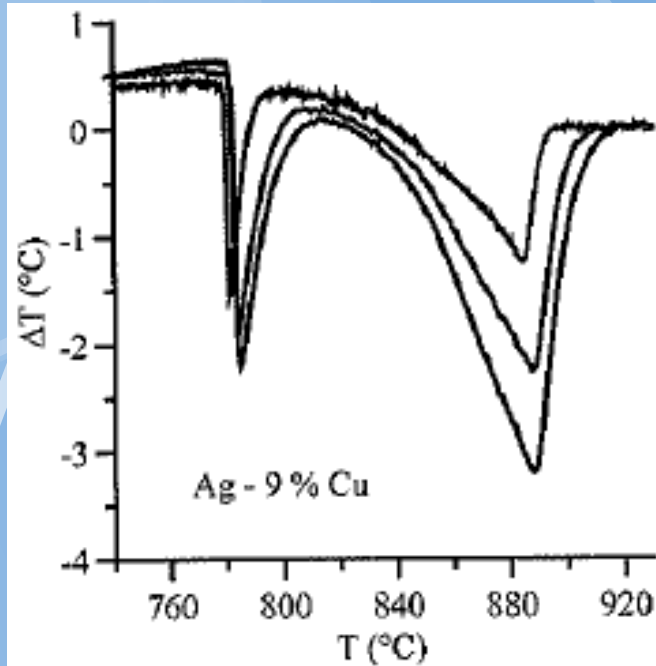


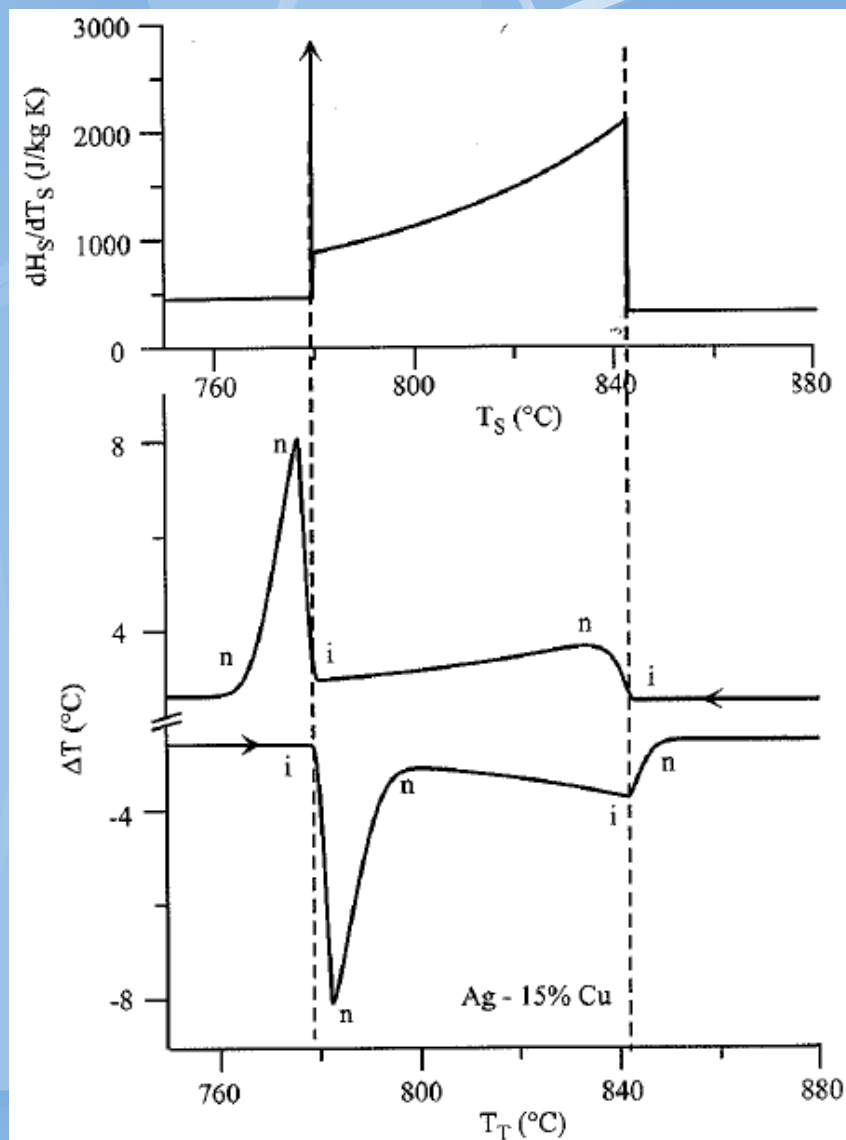
Figure 3.3. Experimental DTA melting scans for a series of Ag-Cu alloys at three different heating rates, 5 K/min (blue), 10 K/min (red) and 15 K/min (black). Note that the small signal for the eutectic melting is absent in the Ag-5 % Cu alloy at the slower heating rates. Note also the absence of a distinct second peak in Ag-23 % Cu. Percentage is by mass.

Snižování rychlosti vede k separaci peaků.



Čisté
eutektikum

Obecná analýza DTA (DSC) signálu



**Simulace signálu
metodou
CALPHAD**

**Teplotní
posuv a
„rozmytí“**

**Reálný signál
odpovídající
simulaci**

*Figure 3.9. dH_S/dT_S vs. T_S (top) and computed DTA scans for melting and freezing at 5 K/min (bottom) for Ag-15% Cu using equilibrium enthalpy. Features on the DTA scans are labeled with: *i* = important or *n* = not important.*

Efekt isotermní prodlevy

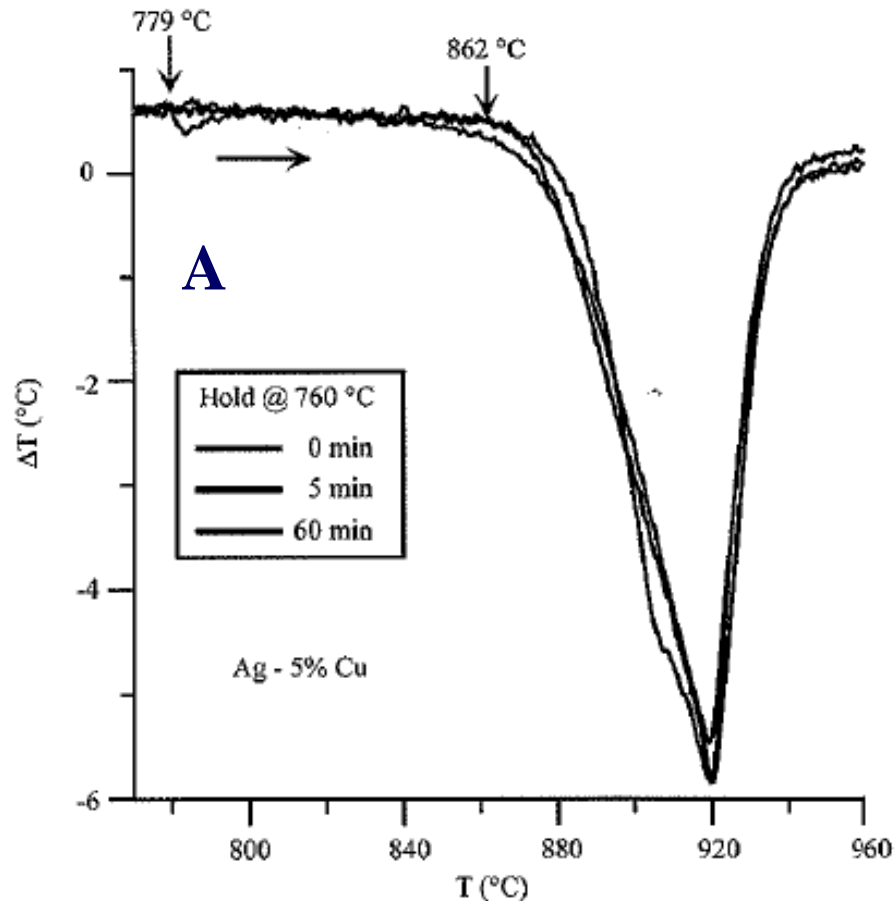


Figure 3.5. DTA signal for melting of Ag- 5 % Cu showing the effect of hold time at 760°C and subsequent heating at 15 K/min.

A...Delší prodleva
na 760stC

Přesnější
určení
solidu

Vliv isothermní prodlevy na rozpuštění Lavesovy fáze

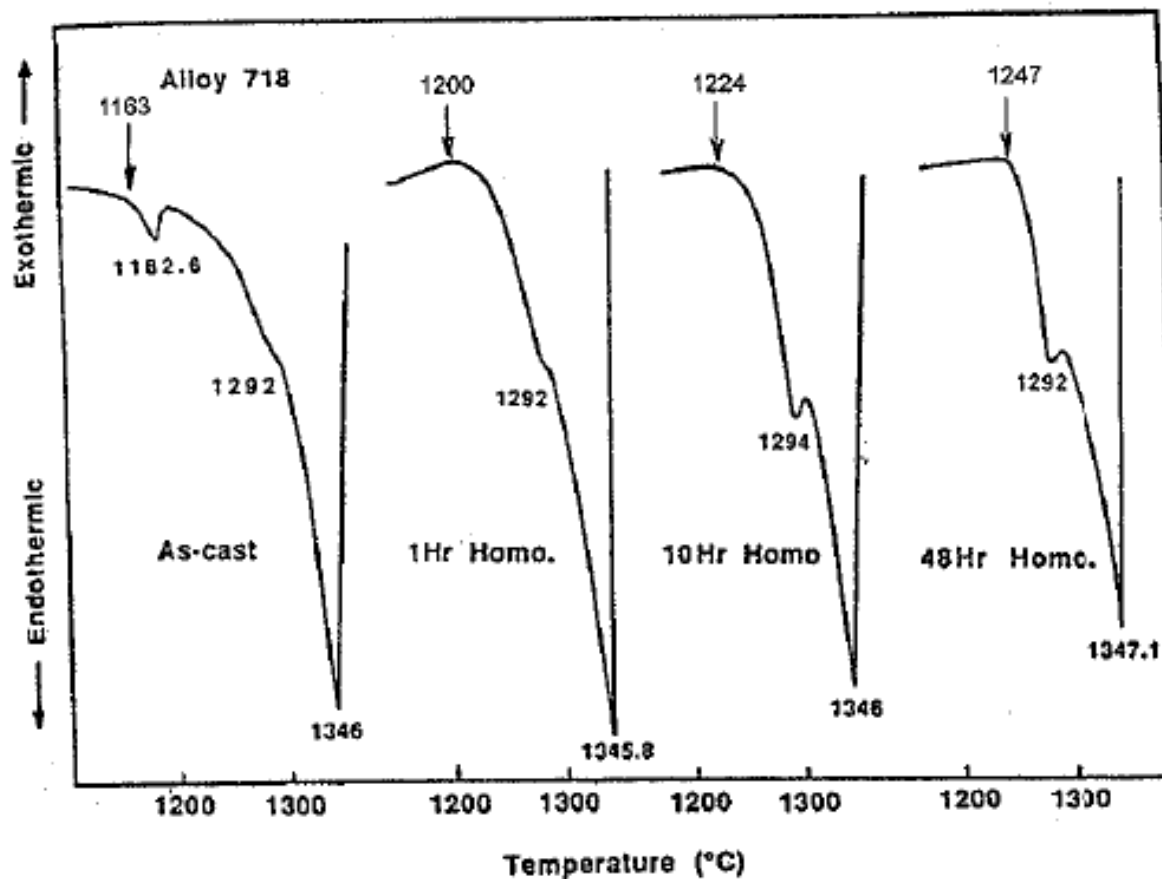
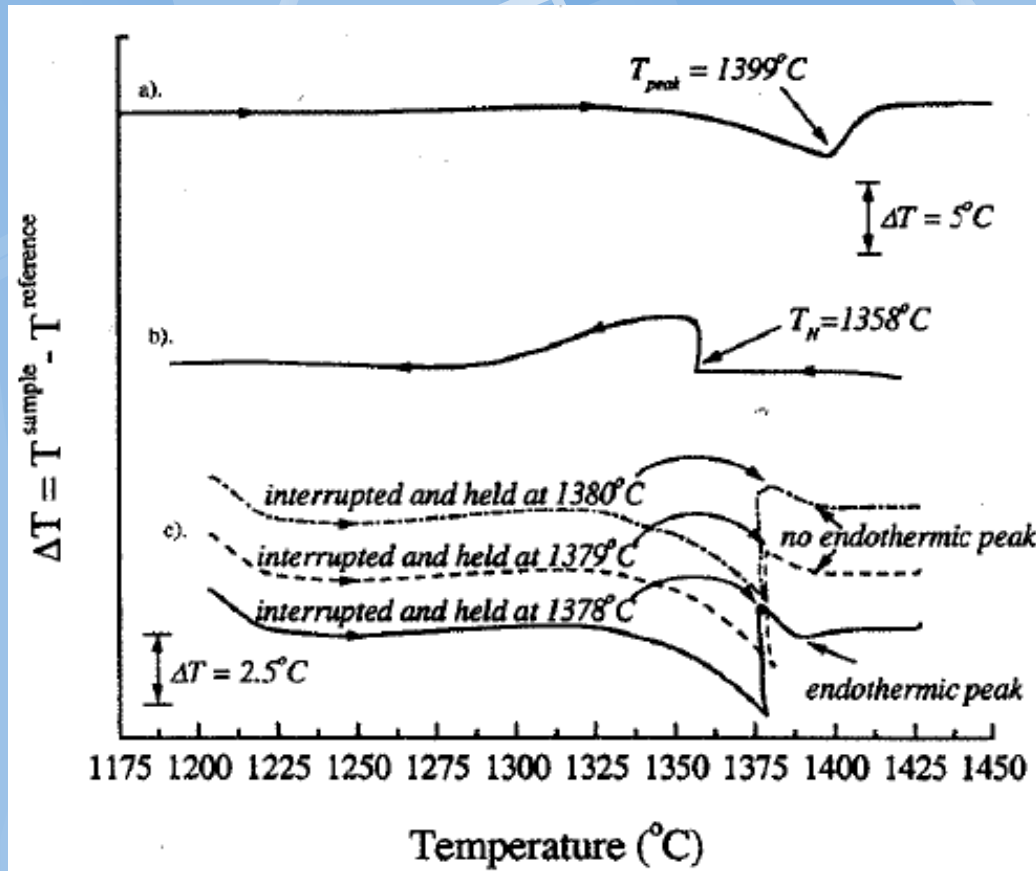


Figure 3.7. DTA signal for Inconel 718 showing the effect of annealing time [91Cao]. With annealing, the $(\text{Fe,Cr})_2\text{Nb}$ Laves phase dissolves and the onset of melting increases from 1163°C to 1247°C.

Upřesnění teploty liquidu, solidu,..



Použitelné pro velmi úzké dvoufázové oblasti

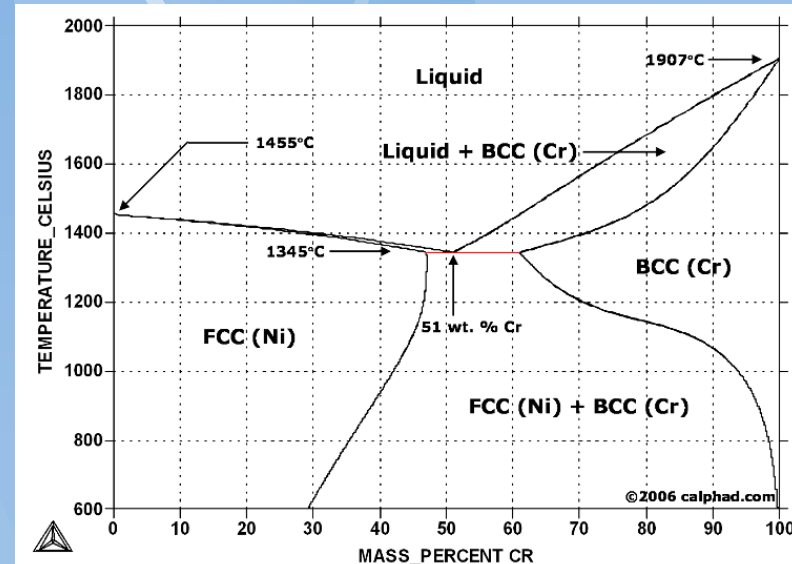


Figure 3.12. a) Normal DTA scan on heating for a small greezing range Ni-base superally; b) Normal DTA scan on cooling. Supercooling has occurred; c) Cycling DTA to determine the liquidus temperature [00Wu].

Rovnovážný výpočet vs. Sheil-Gulliver aprox.

Rovnovážný výpočet

Rovnováha v každém okamžiku (chladnutí i ohřevu).

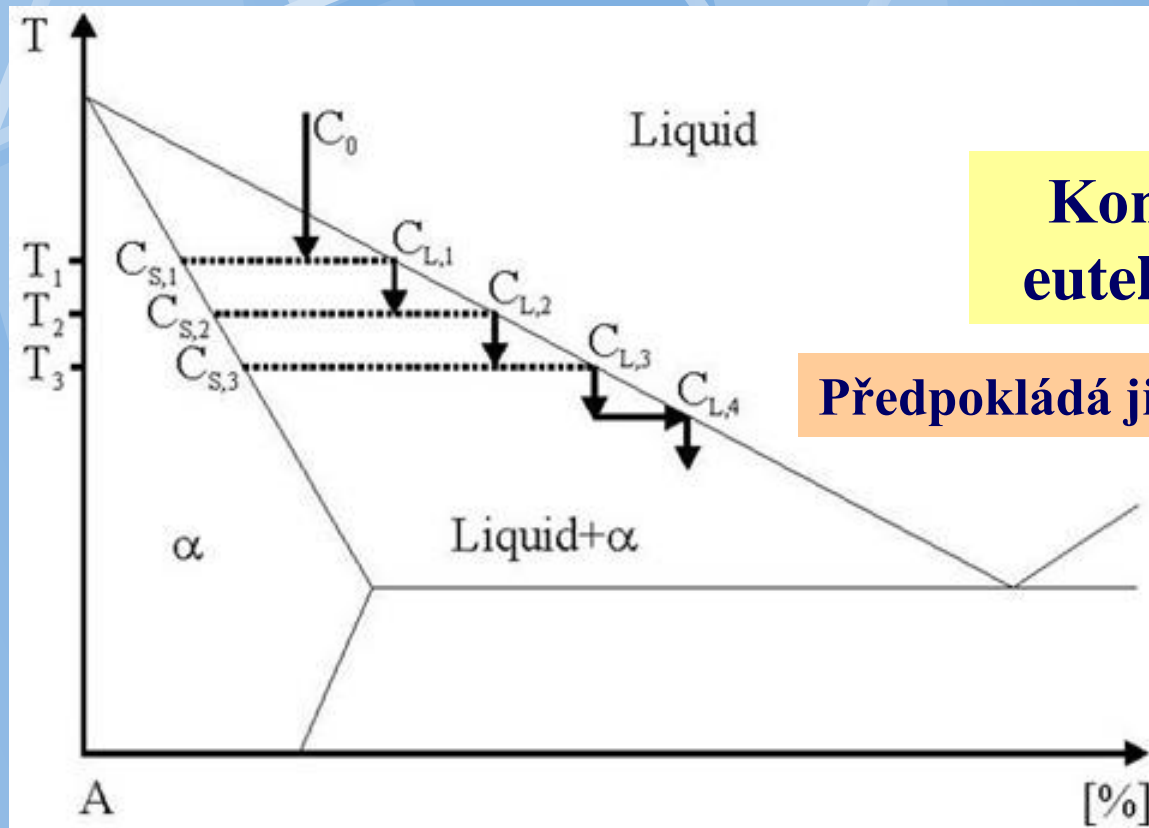
Soulad s experimentem při nízkých rychlostech

Sheil aproximace

Vylučování tuhé fáze (bezdifúzní) z kapalné (nekonečná difúze) s definovaným podchlazením nebo množstvím odnímaného tepla

Soulad s experimentem při vyšších rychlostech změny teploty

Scheil-Gulliver aprox.



**Končí v
eutektiku**

Předpokládá jisté podchlazení

Scheme of Scheil solidification of a hypothetical Fe-C alloy. During solidification the actual liquid phase, beginning with C_0 , is undercooled and solidifies according to the lever rule enriching the liquid phase with solute atoms

Sheil vs. equilibrium

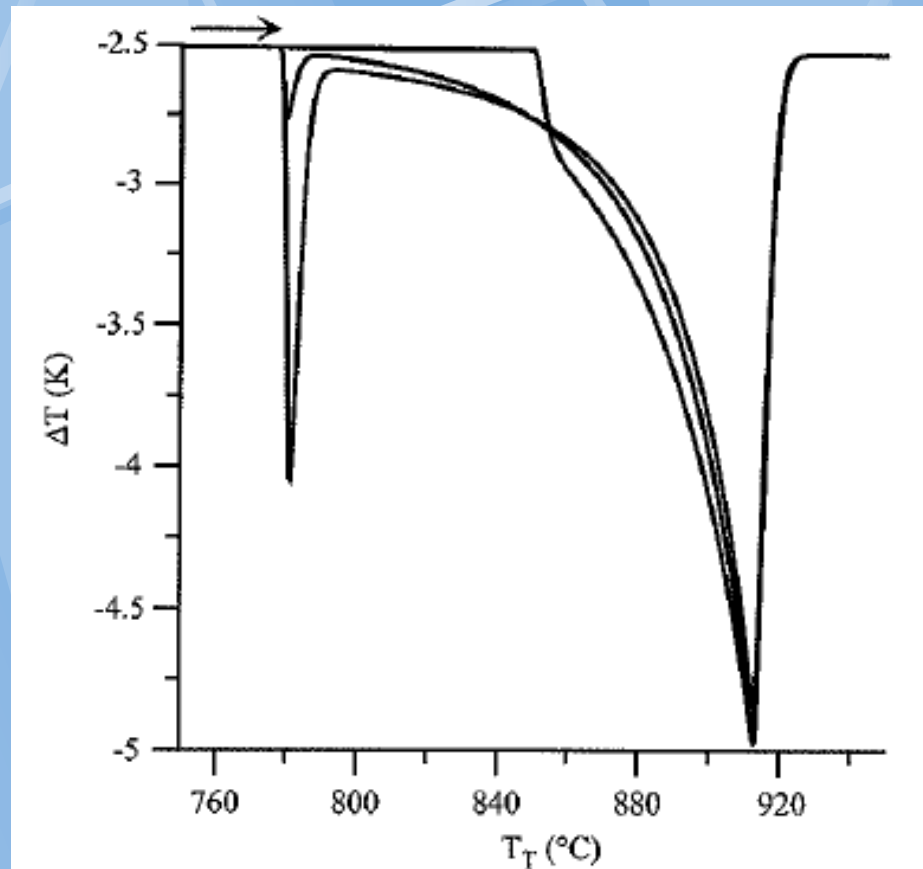


Figure 3.6. Computed DTA curve for an enthalpy vs. temperature relation derived from a back diffusion model of solidification at 5 K/min of Ag 5 % Cu is shown blue. $D_S = 1 \times 10^{-14} \text{ m}^2 / \text{s}$, $\lambda_2 = 3.8 \times 10^{-5} \text{ m}$. The equilibrium curve is black and the Scheil is red. The peak eutectic signal at approx. 780°C is intermediate between that for the Scheil and equilibrium cases but is not as small as the measured eutectic signal with no annealing in Figure 3.5.

Tvar signálu DTA (DSC) I-s binární rovnováhy

k...rozdělovací koeficient

$$k = x_1^s / x_1^l$$

Přerozdělovaná složka

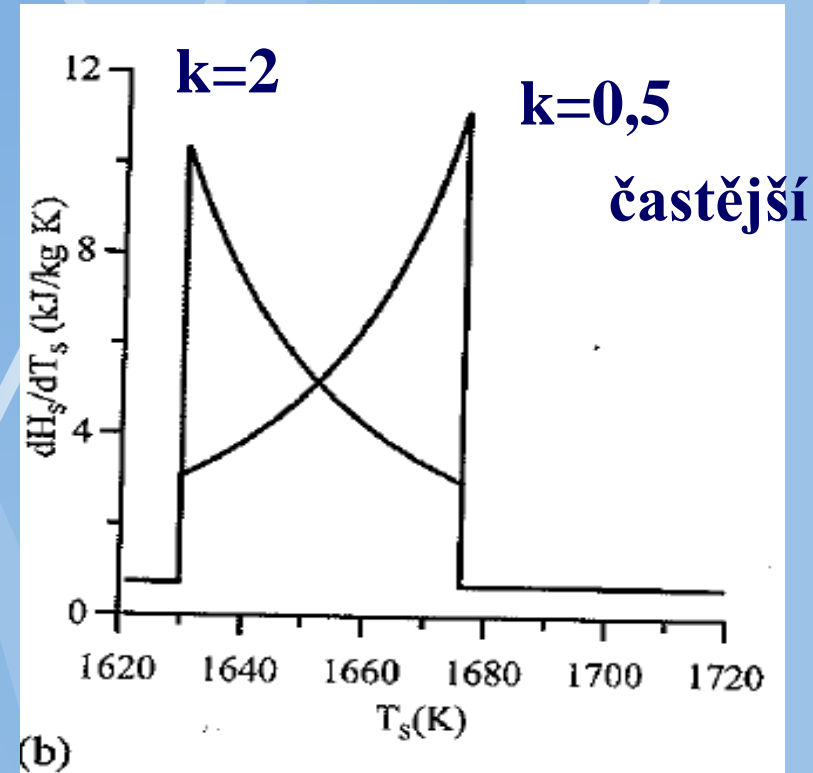
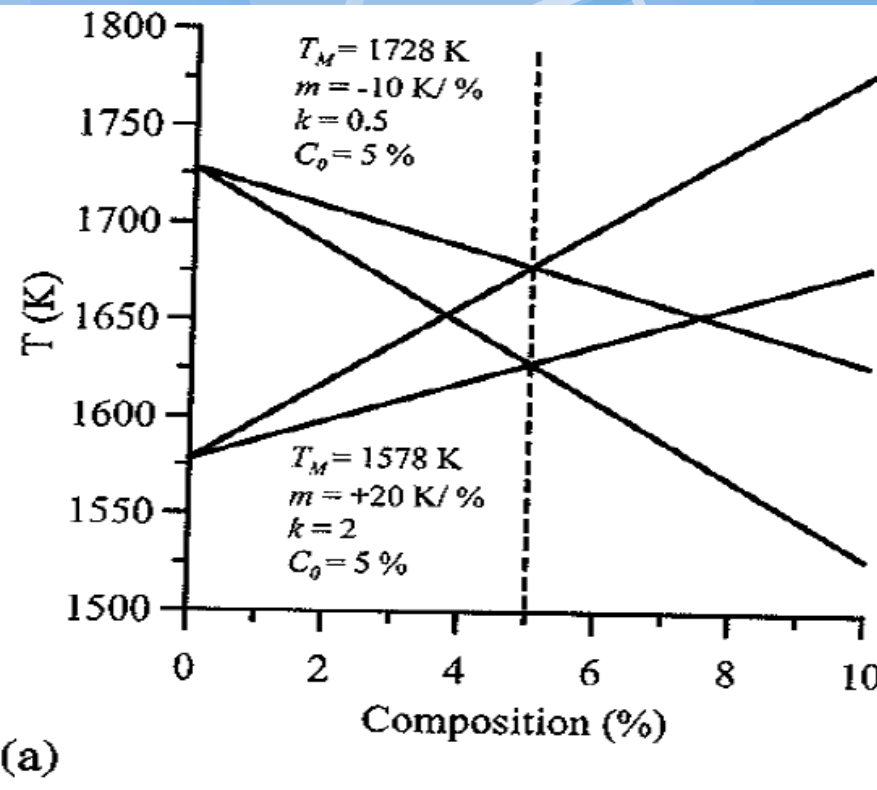
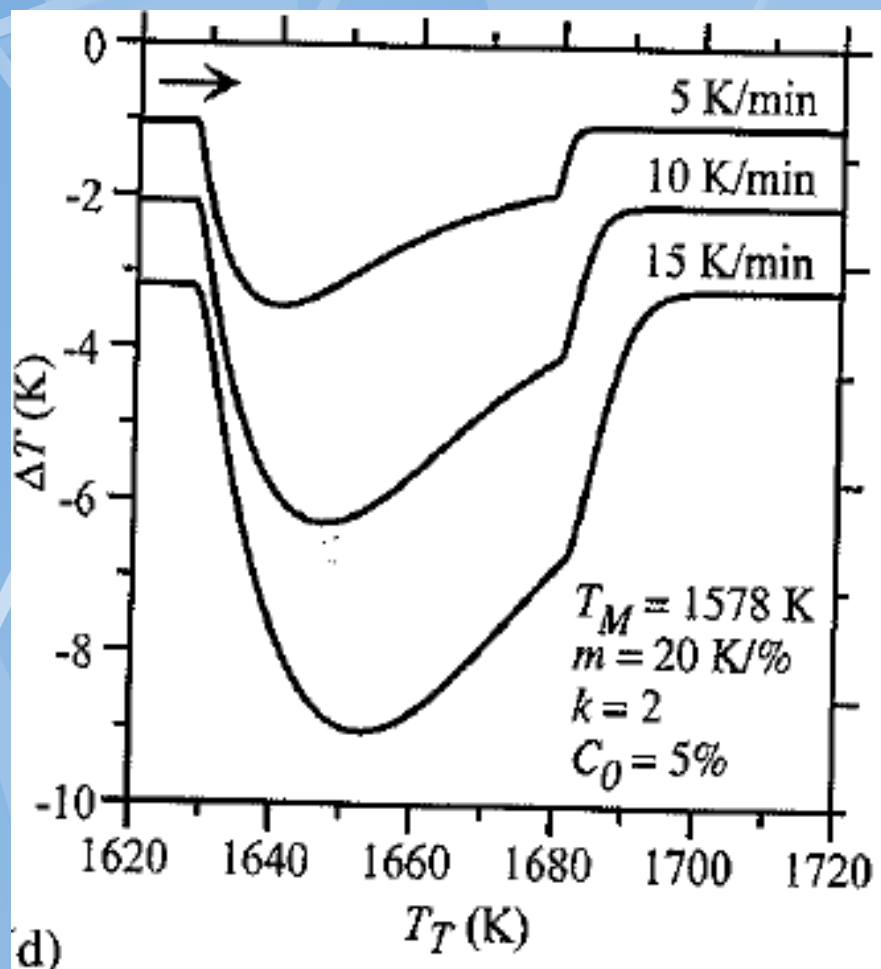
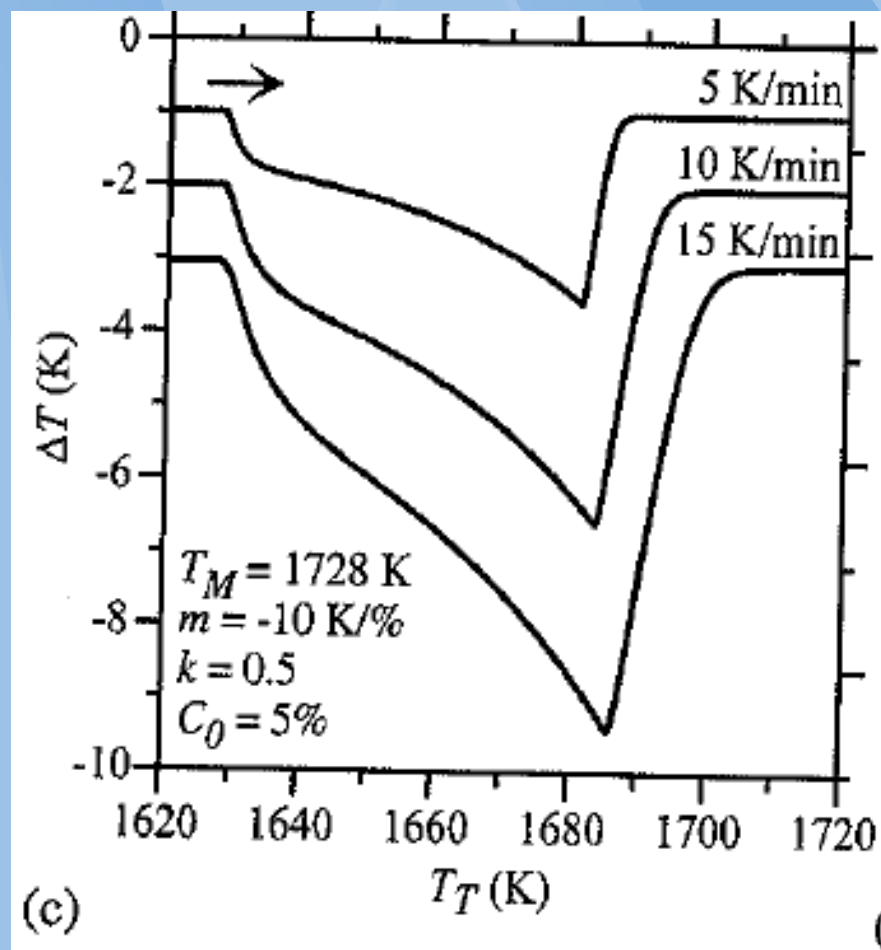


Figure 3.13. Comparison of two hypothetical alloys with identical heat of fusion, liquidus and solidus temperatures but differing having $k < 1$ and $k > 1$. a) Phase diagram, b) dH_S / dT_S for $k < 1$ (black) and $k > 1$ (red), c) DTA for $k < 1$ and d) DTA for $k > 1$. For $k < 1$, the latent heat is released higher in the



Častější případ (eutektika)

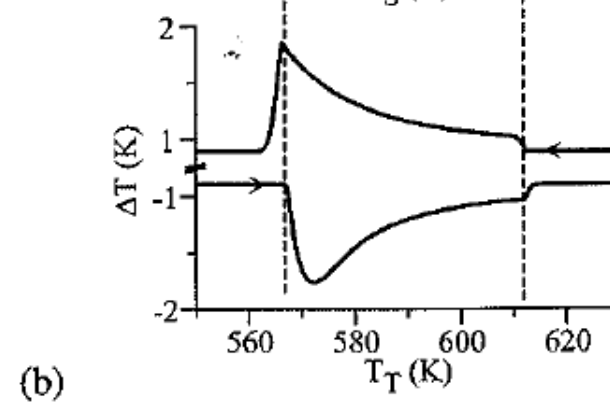
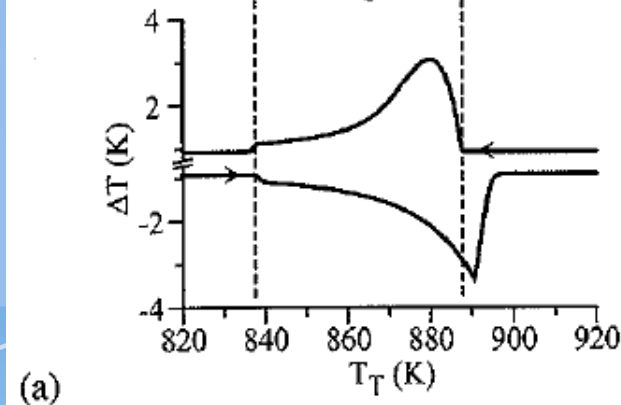
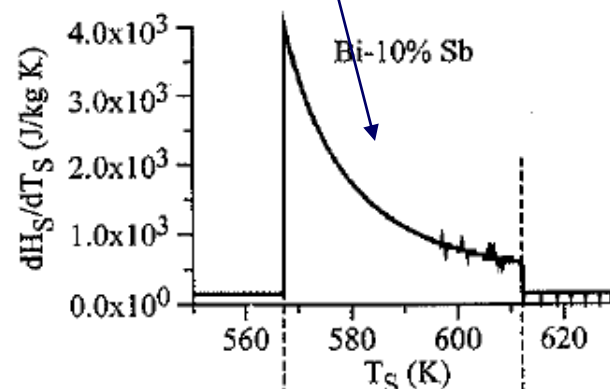
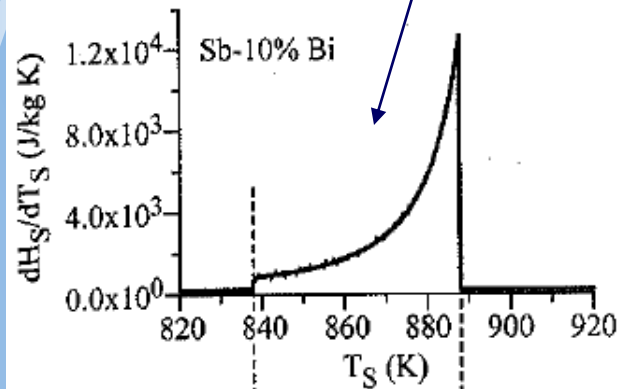
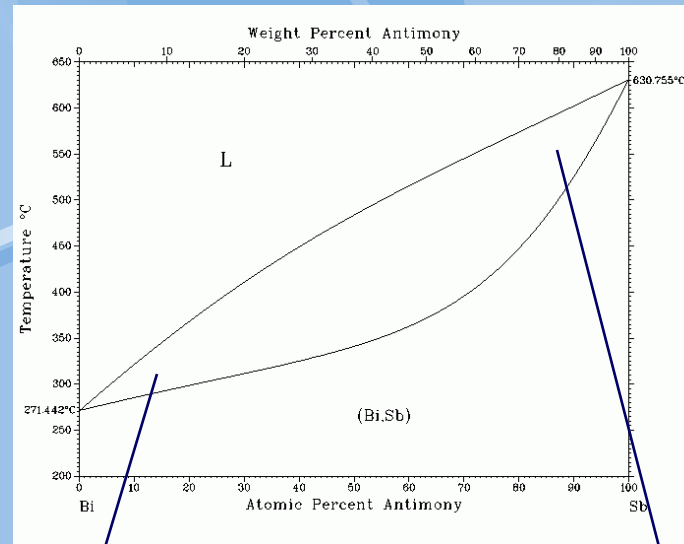
Méně časté (peritektika)

Sn-Bi

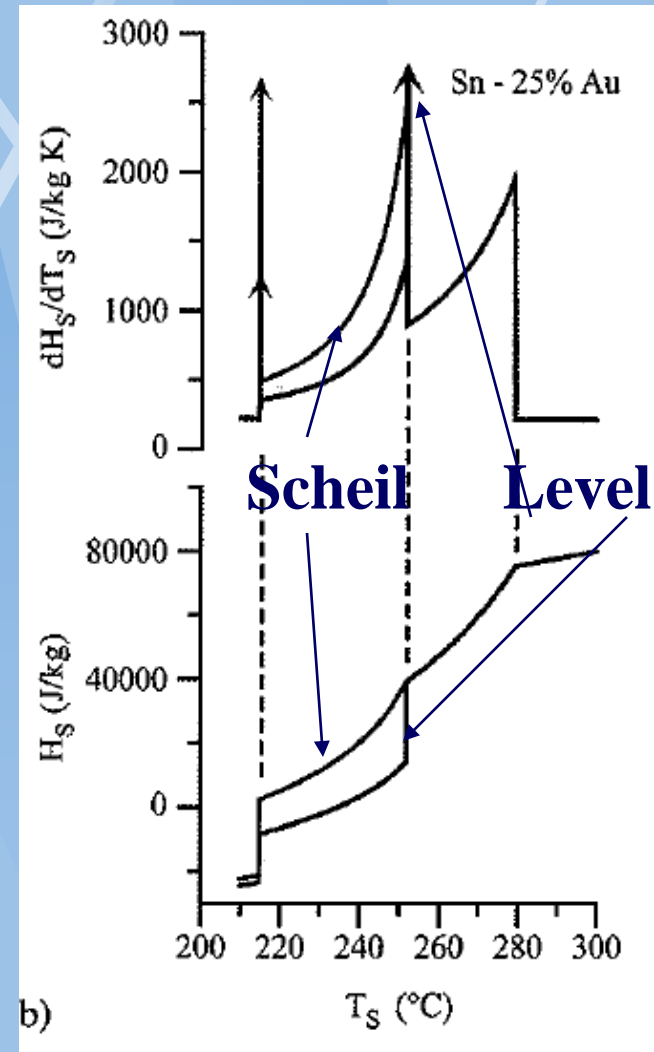
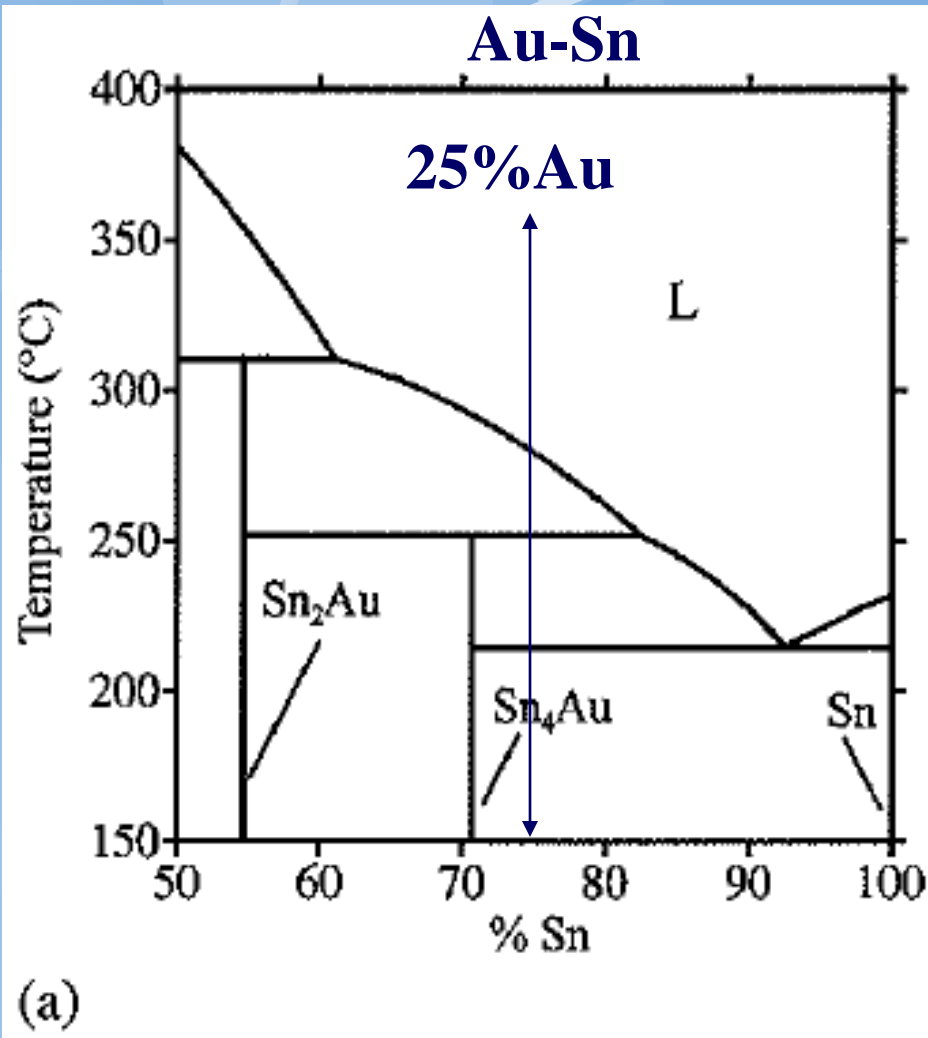
CALPHAD DATABASE

Sb

Bi

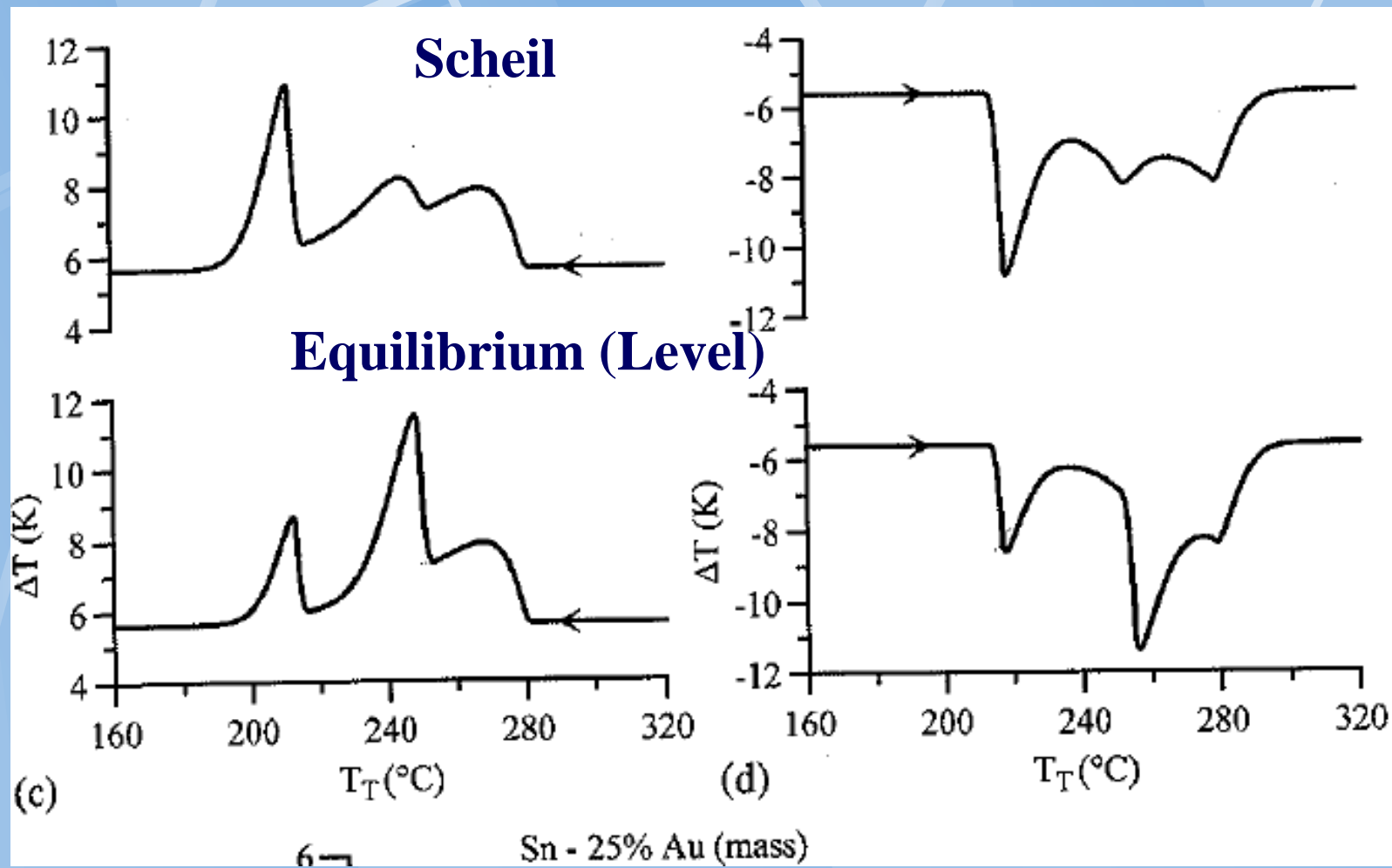


Eutektické a peritektické reakce



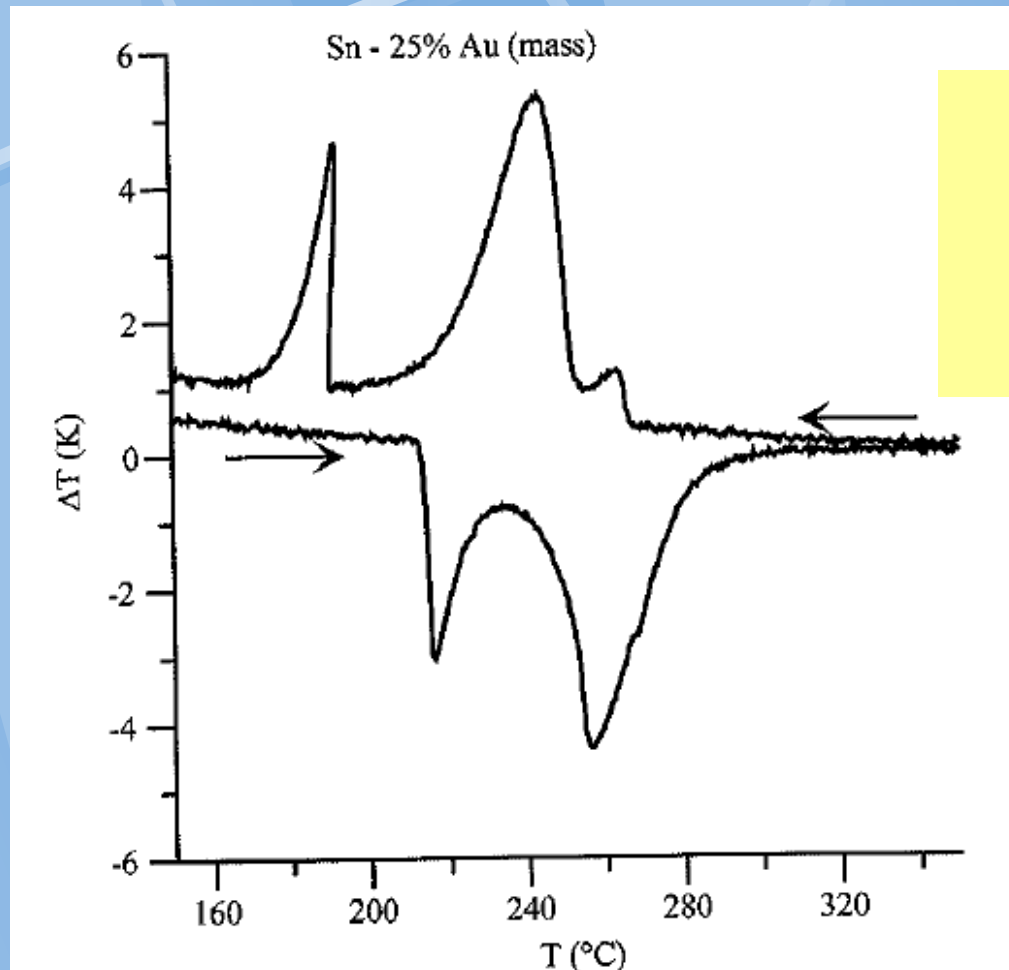
Pozn.: Equilibrium výpočet = Level

Vypočtený signal Au-Sn s uplatněním přístrojových konstant



S přístrojovými parametry pro přenos tepla a jeho
zpoždění v přístroji

Reálný signál Sn-25Au

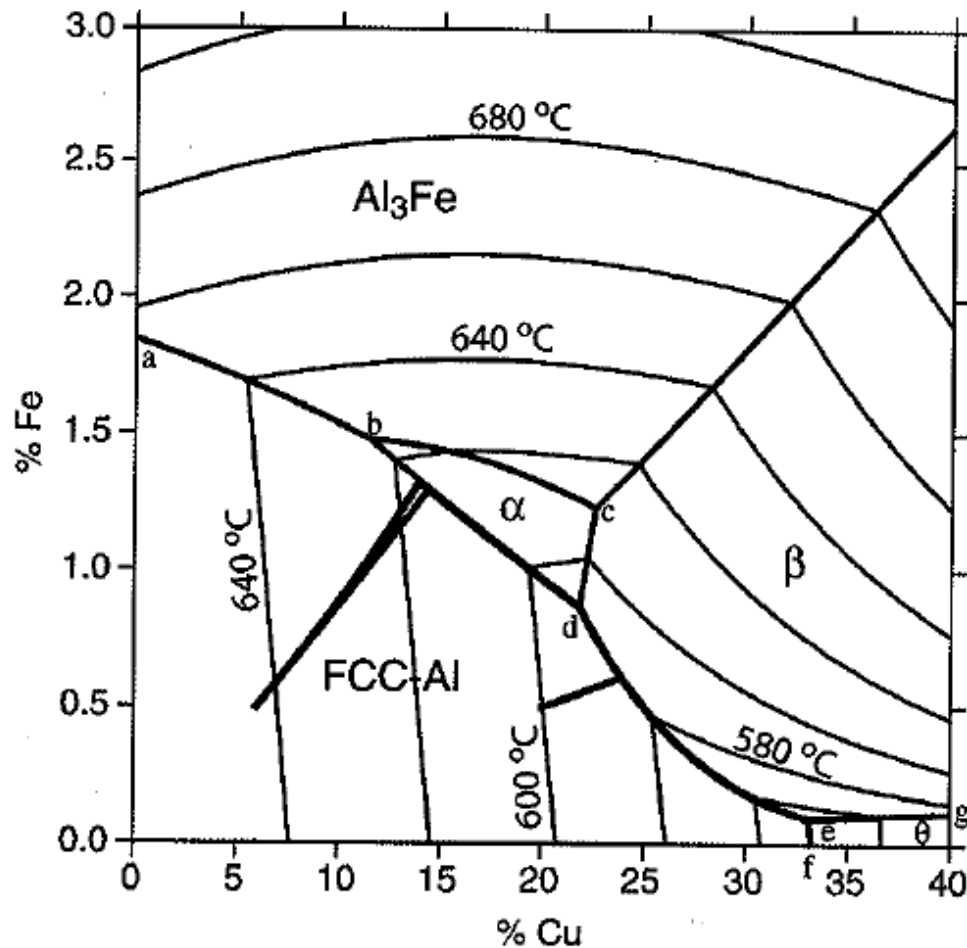


**Signál
odpovídá
spíše
rovnováze**

e) Experimental melting and freezing curves at 5 K/min.

Ternární slitiny

Liquidus surface of Al-rich corner of Al-Cu-Fe alloy



Al - 6% Cu - 0.5% Fe

Al-20 wt% Cu- 0.5% Fe

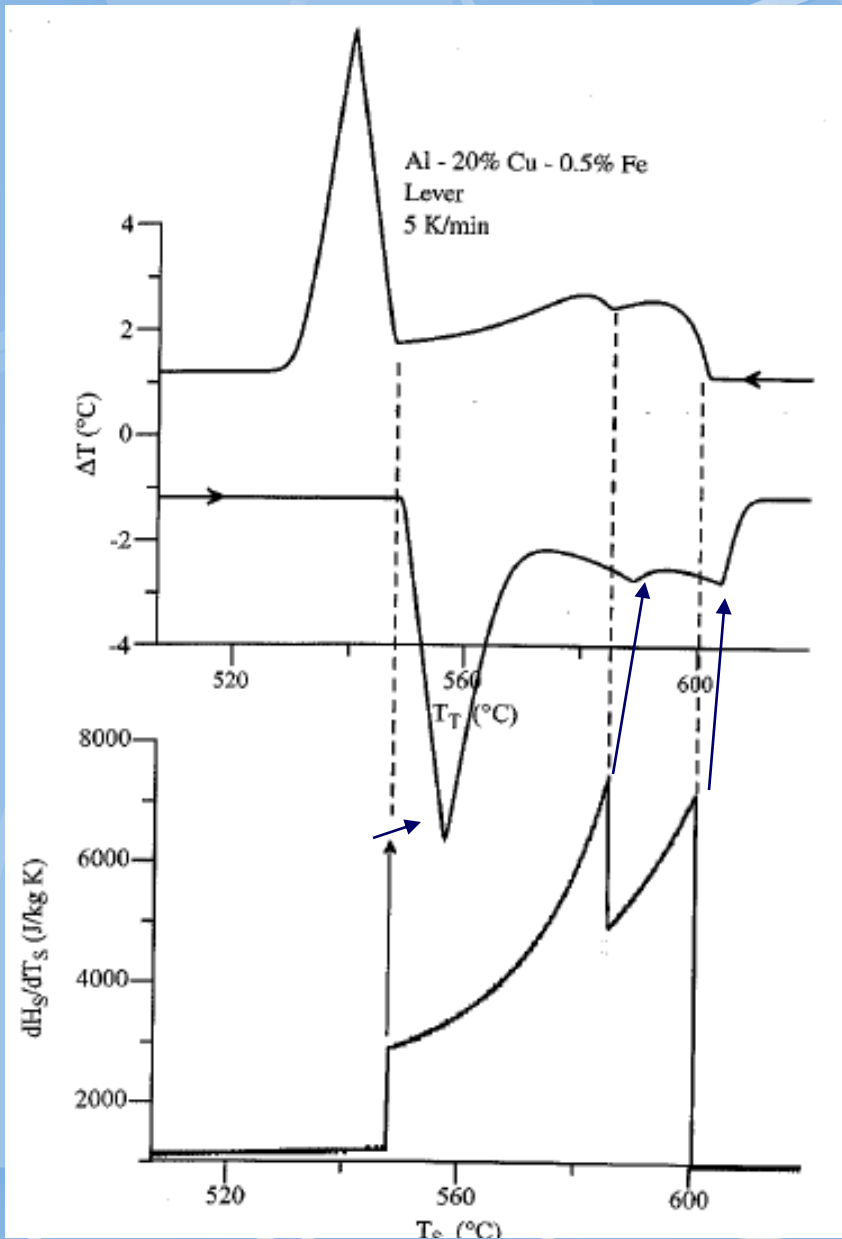
**Scheil a Lever
aproximace**

Al-20Cu-0,5Fe

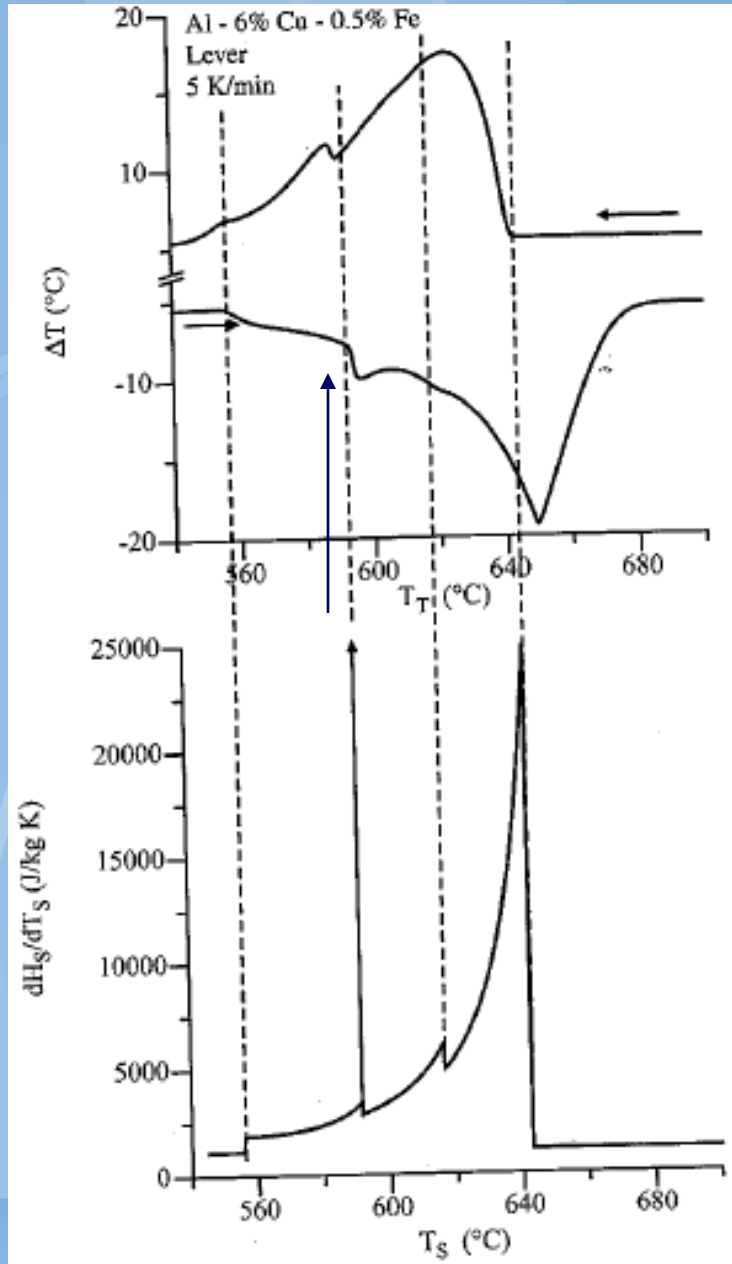
Reálný
signál

$L \rightarrow \text{FCC},$
 $L \rightarrow \text{FCC} + \text{Al}_7\text{Cu}_2\text{Fe},$
 $L \rightarrow \text{FCC} + \text{Al}_7\text{Cu}_2\text{Fe} + \text{Al}_2\text{Cu}.$

Lever
(rovnovážný
výpočet



Al-6Cu-0,5Fe – rovnovážná simulace



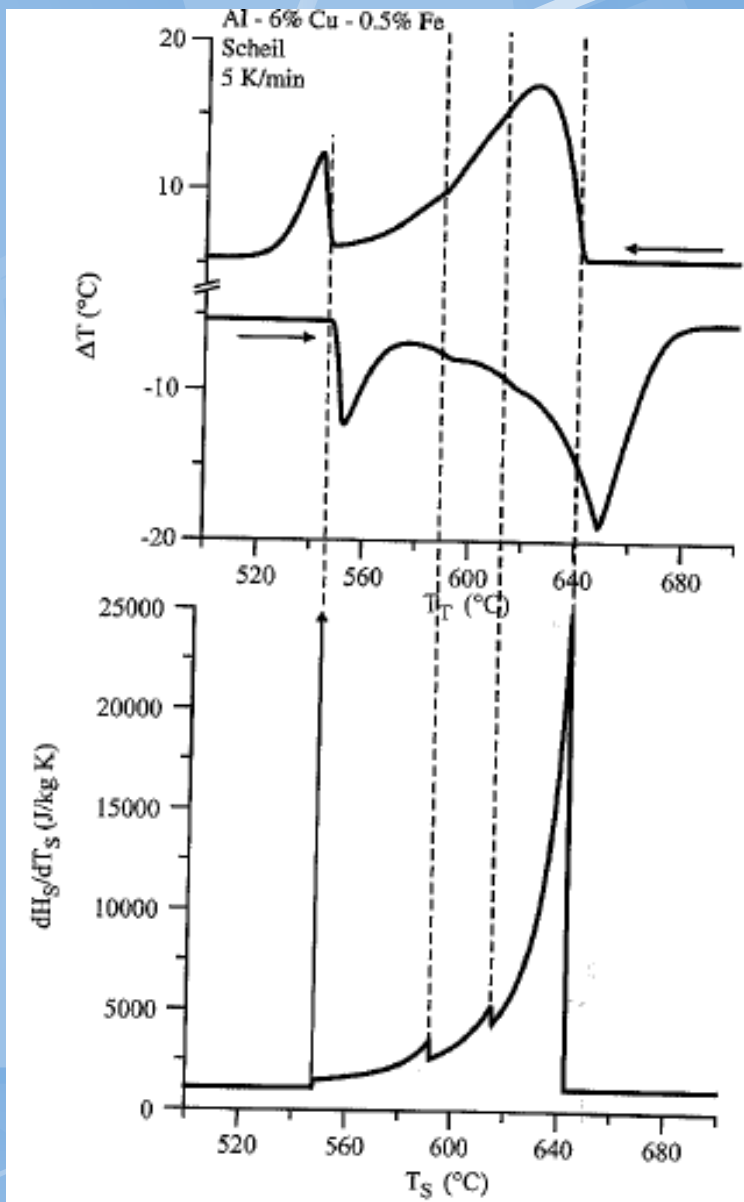
**Reálný
signál
5K/min**

L→FCC,
L→FCC+Al₆(Fe,Cu),
L+Al₆(Fe,Cu)→Al₇Cu₂Fe+FCC (invariant); Lever path only.

**Lever
(rovnovážný
výpočet**

Vyhovuje

Al-6Cu-0,5Fe – nerovnovážná simulace



**Reálný
signál
15K/min**

**Scheil (nerovnovážný
výpočet)**

Vyhovuje

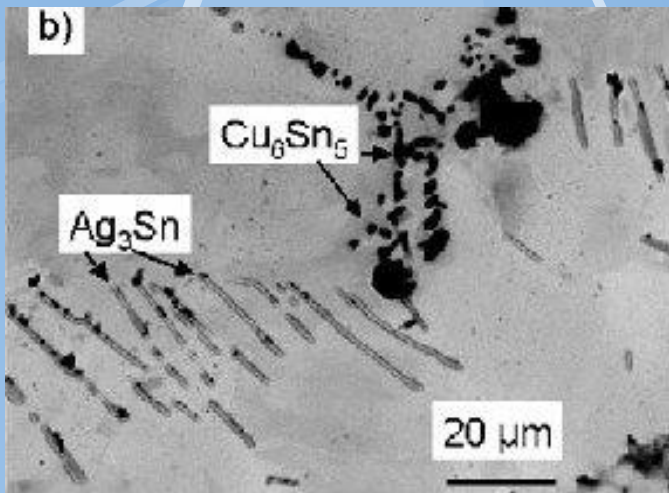
Přístrojové parametry

Příklad konstant tepelného zpoždění

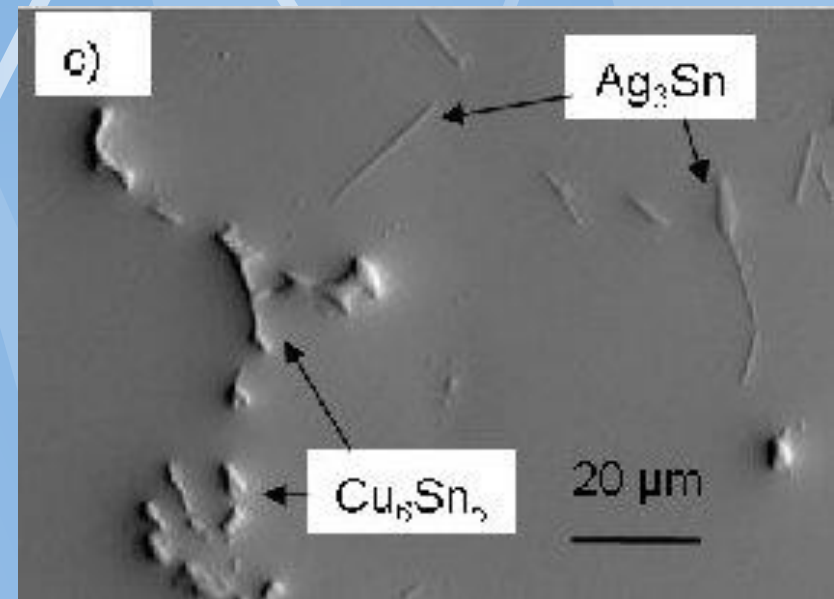
	Sn (232°C)			Ag (961°C)			Ni (1453°C)		
Mass (g)	0.163			0.237			0.180		
Heating rate (K/min)	5	10	15	5	10	15	5	10	15
$t_{S,C}$ (s)	13.5	15.3	15.9	6.2	6.7	6.7	6.5	6.0	5.5
$t_{W,C}$ (s)	34.5	29.2	26.3	13.0	12.7	13.1	5.1	5.0	4.7
$t_{T,C}$ (s)	27.6	18.9	17.0	14.5	12.4	11.7	7.4	6.5	6.7
$t_{W,C} / t_{S,C}$	2.56	1.91	1.65	2.10	1.90	1.96	0.78	0.83	0.85

Vícesložkové slitiny

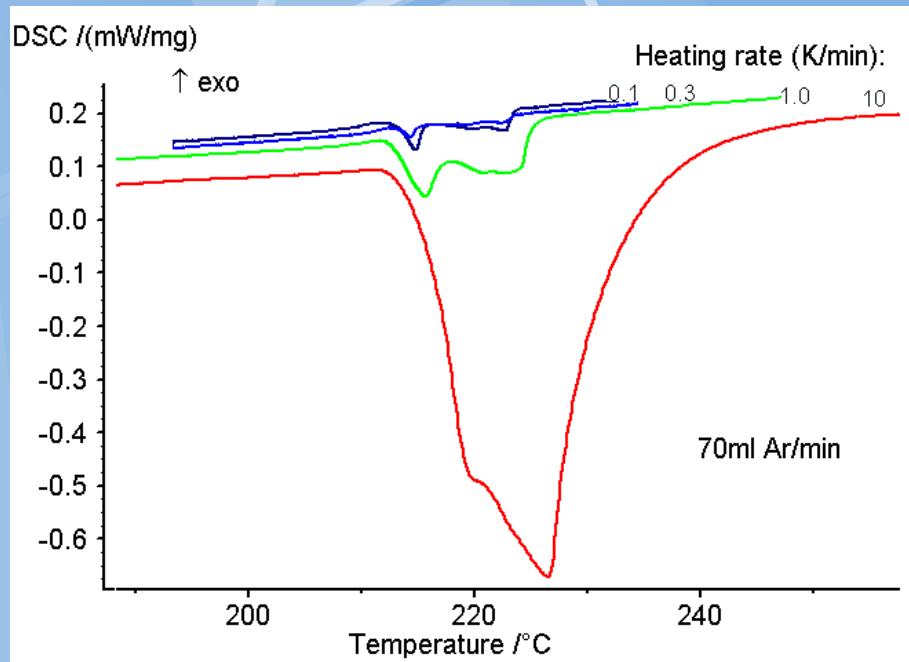
Slitiny na bázi Sn bez olova



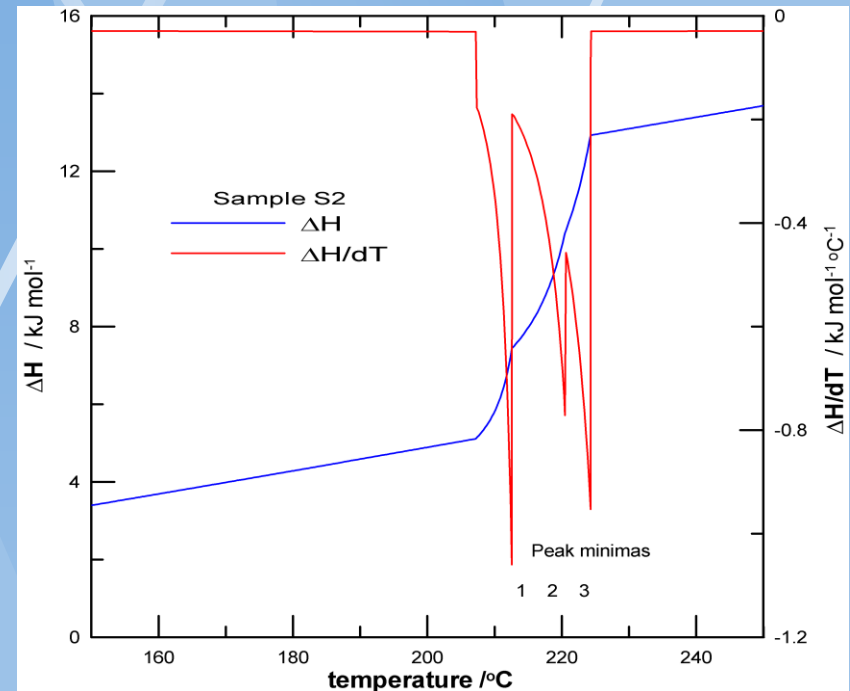
Microstructura slitiny Sn-
3.5%Ag-0,7%Cu-1%Bi.
Světelná mikroskopie (b), SEM
(c).



Simulace DSC křivek

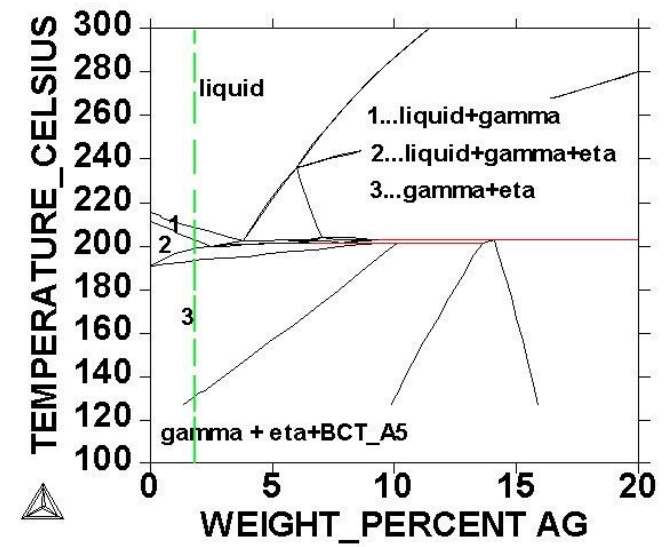
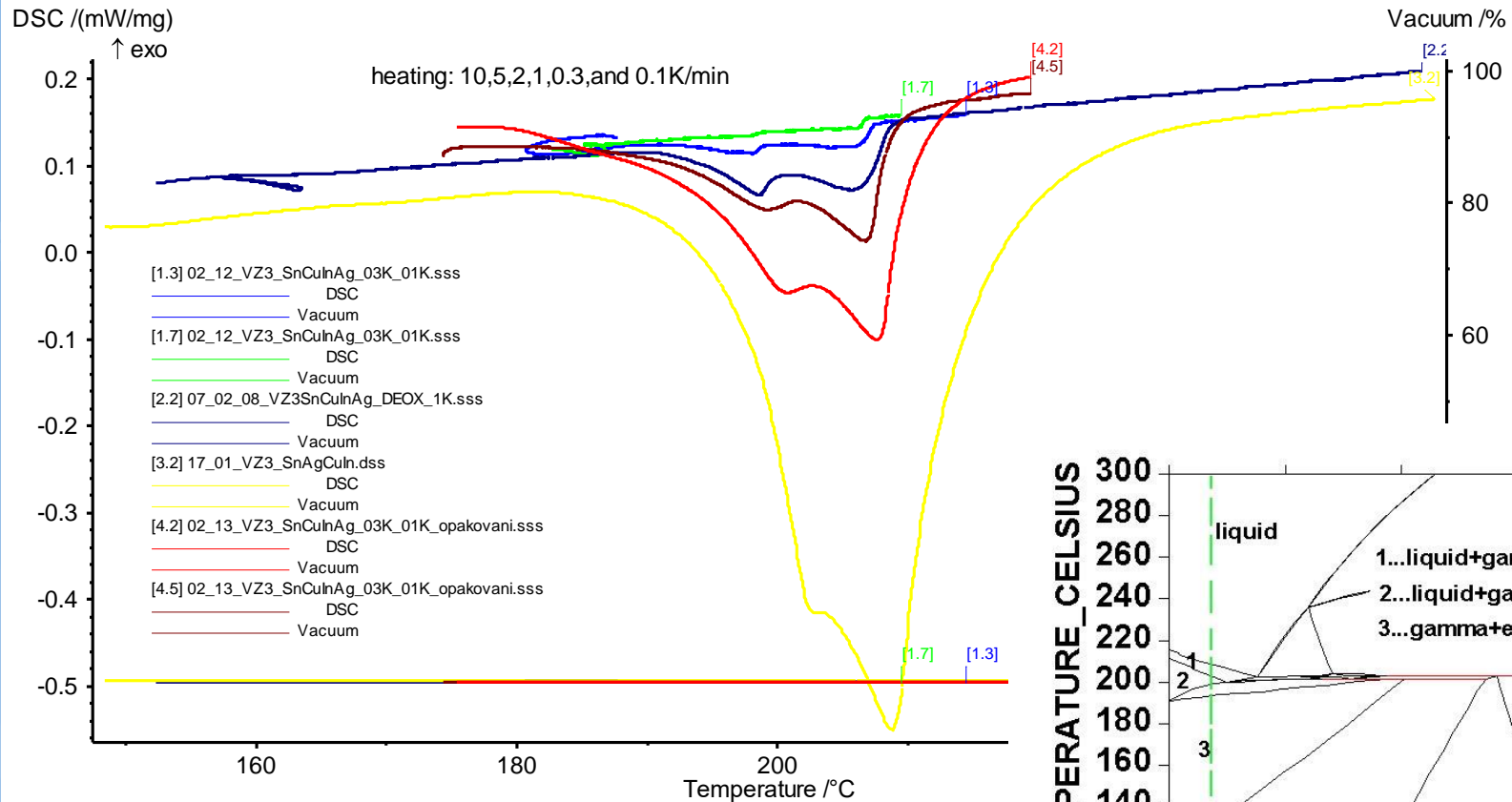


Experimentálně naměřený DSC signál pro různé rychlosti ohřevu slitiny Sn-3.5%Ag-0,7%Cu-1%Bi.



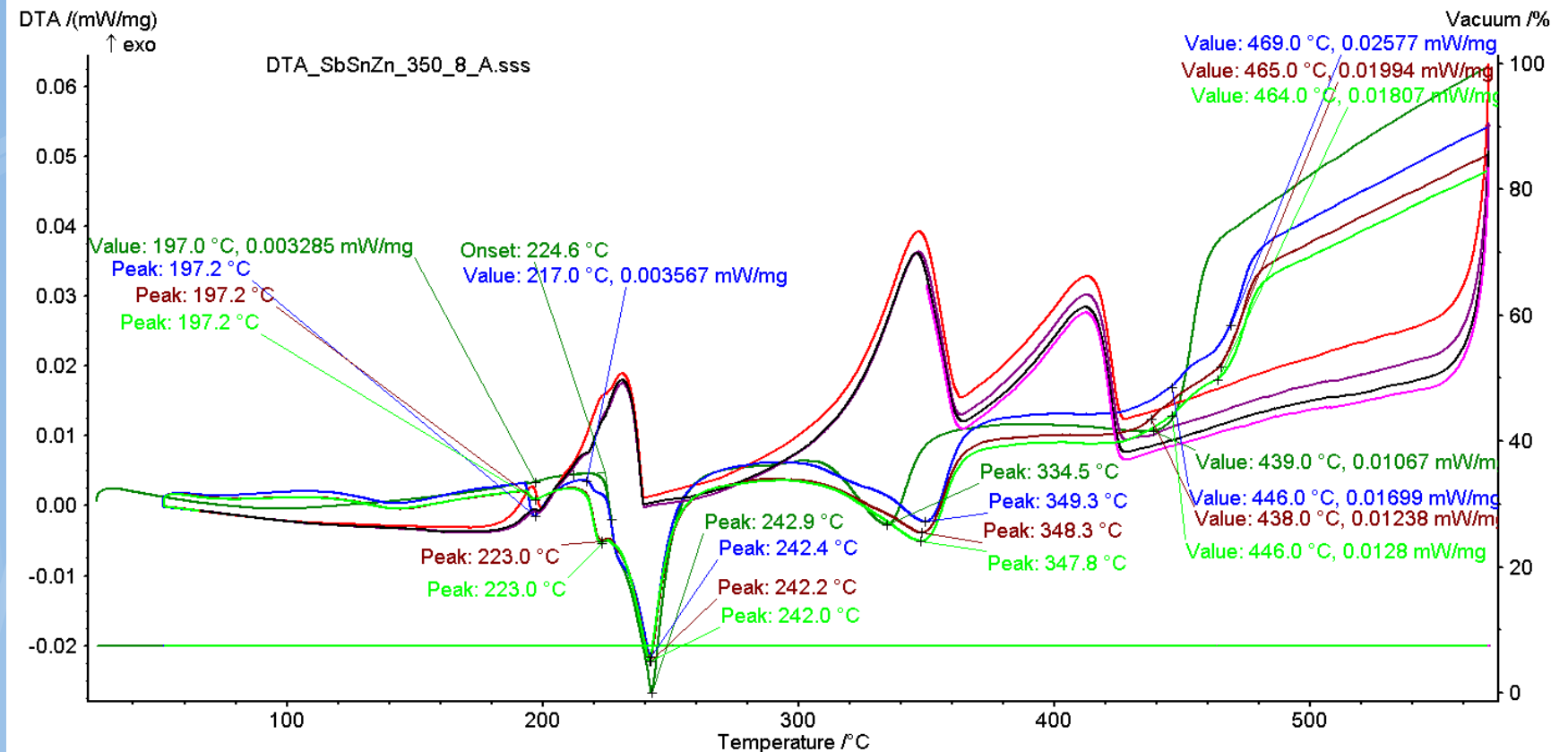
Vypočtená závislost entalpie a tepelné negarivní kapacity sledované slitiny.

Termická analýza a temod. rovnováha



DSC signál slitiny Sn-0,7wt%Cu-1,5%Ag-9,5%In při různých rychlostech ohřevu v korelaci s fázovým diagramem.

Diskuze



signál DTA slitiny SbSnZn

The Calphad Approach

Phase Equilibria & Thermodynamics

Experiments

DTA, Metallography,
X-ray Diffraction,
Calorimetry, EMF,
Vapor Pressure

Physics-based
Model Functions
with *Adjustable*
Parameters

Theory

Quantum Mechanics
Statistical Thermodynamics

Parameter
Optimization
for *Thermodynamic*
Description

Thermodynamic
Database

Applications
Solidification,
Phase Transformation Kinetics,
...

Diffusion

Experiments

Tracer, Intrinsic,
Chemical (Interdiffusion)

Theory

Atomistic
Calculations

Parameter
Optimization
for *Diffusion Mobility*
Description

Diffusion Mobility
Database

Thermodynamic
Factor

Thermodynamic
Factor

