Audio test:

Termická analýza

Teplotně modulovaná DSC (tmDSC)

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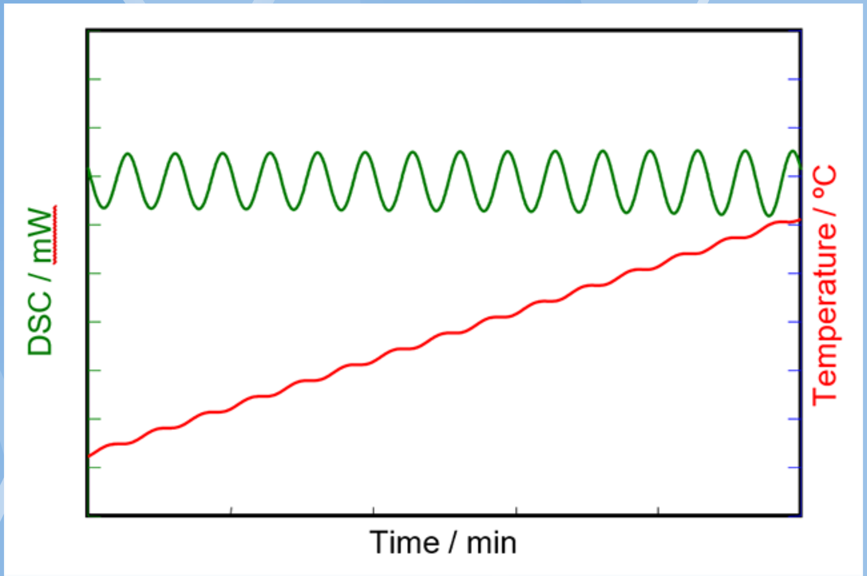
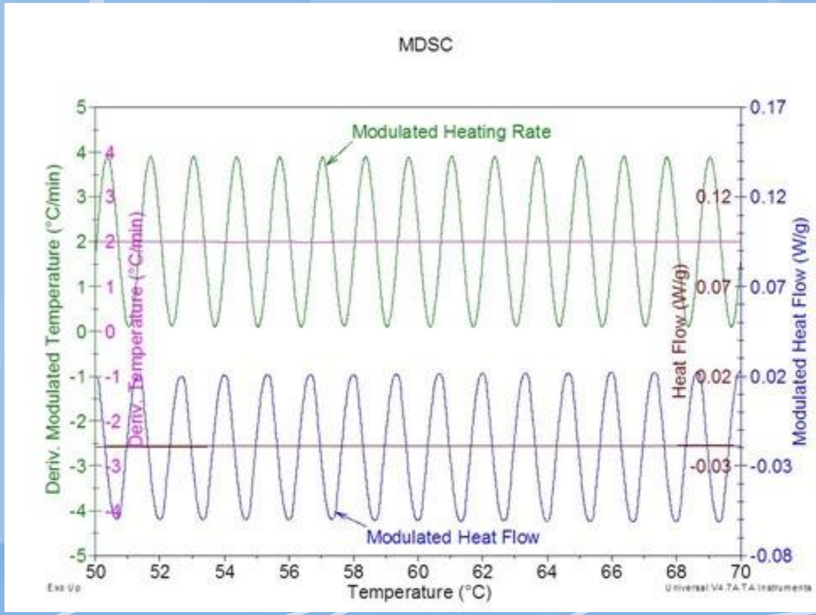
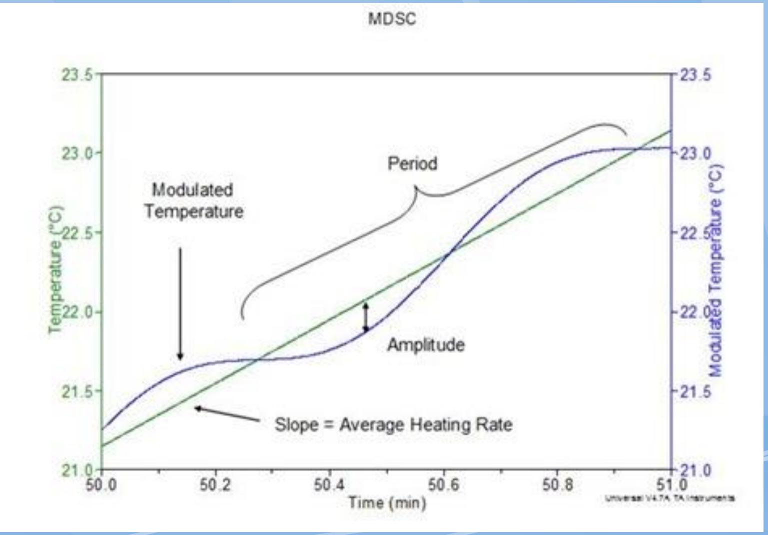
Brno, prosinec 2011

Modulated temperature

Temperature Modulated DSC (TM-DSC)

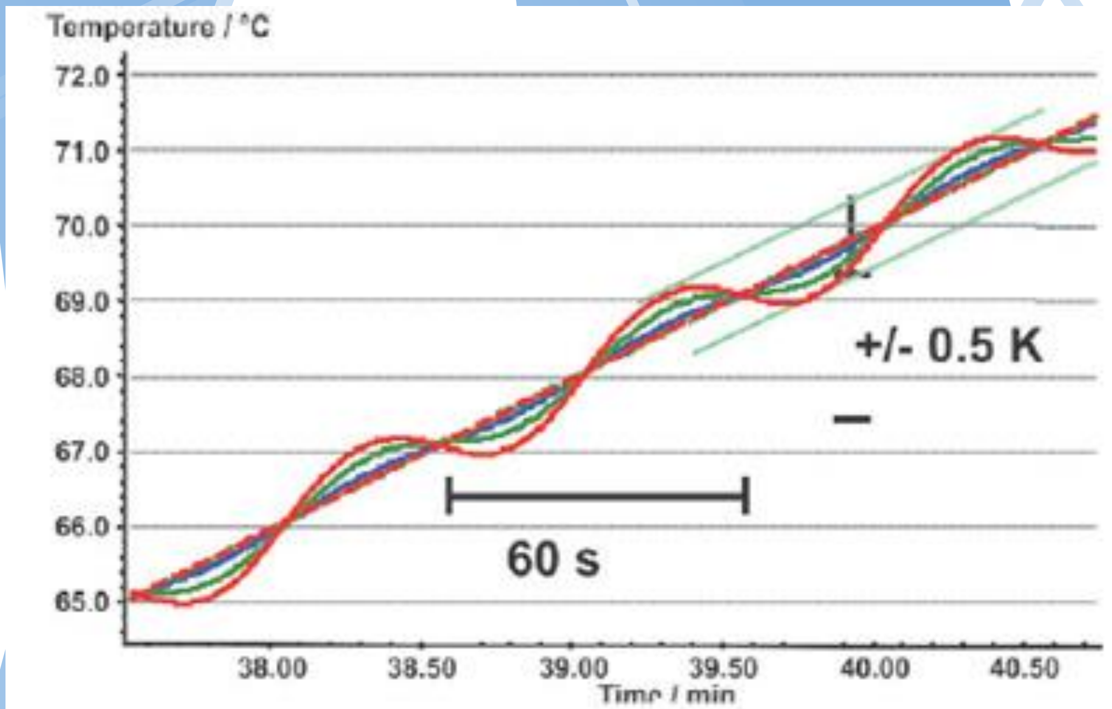






Teplotně modulovaná DSC

$$T(t) = T_0 + HR.t + A.\sin(\omega\, t) \dashrightarrow dT/dt = HR + A\,\omega\,\cos(\omega\, t)$$



Stejná instrumentace jako pro DSC

Není ovlivněno driftem baseline

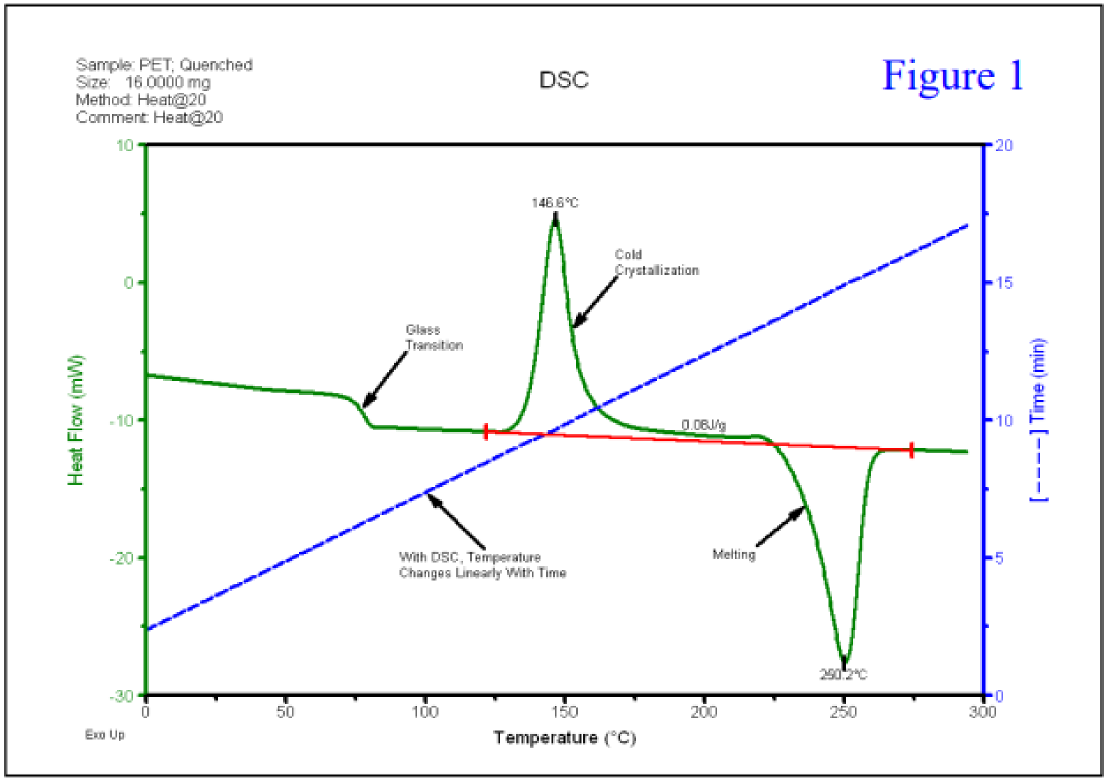
Měřit lze i při T_0=konst.

Lze rozlišit reverzibilní a nereverzibilní děje.

Figure 1. Modulated heating rate with a period of 60 s and amplitudes of 0.1, 0.3 and 0.5 K (underlying heating rate: 2 K/min).

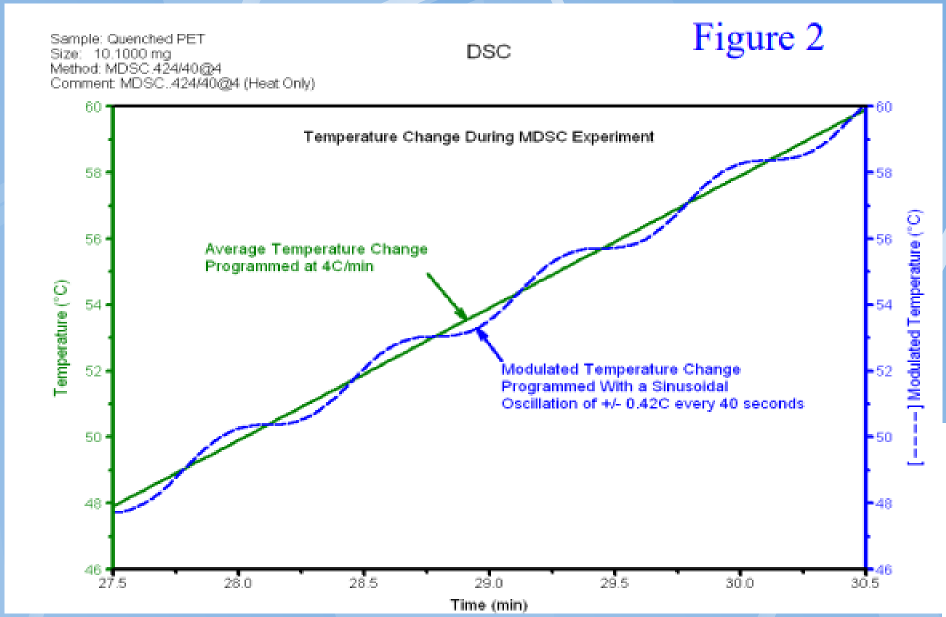
Normální DSC

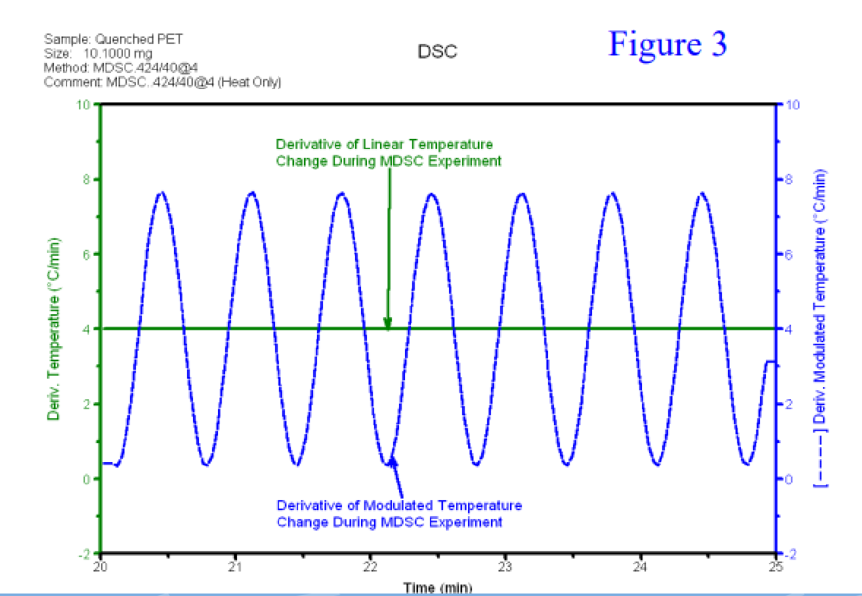
the sum of all heat flows occurring at any point in temperature or time. An example of such a DSC experiment is shown in Figure 1 for a sample of Polyethylene Terephthalate (PET) that had been quench-cooled from a temperature above its melting point.

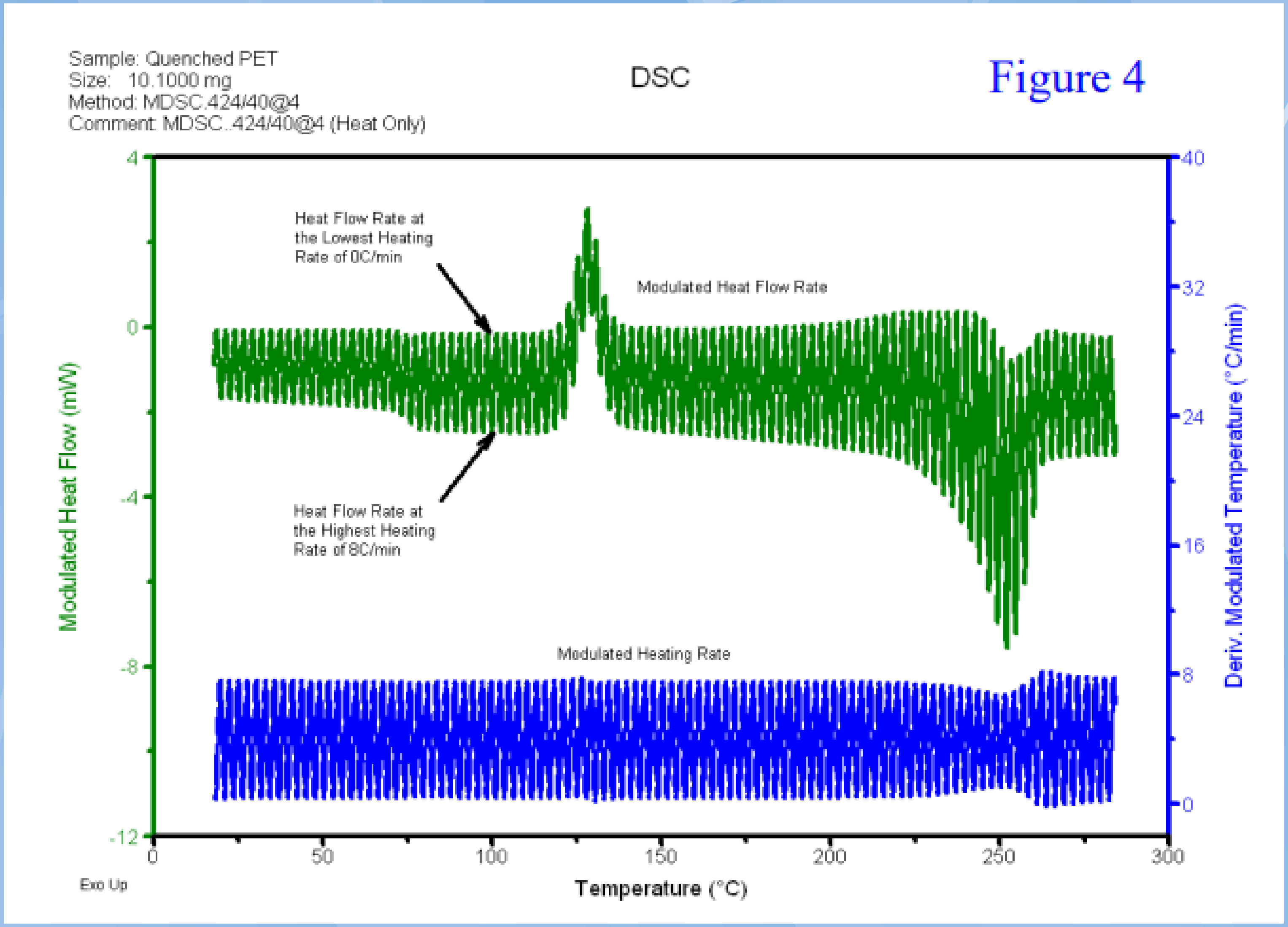


[TP_006_MDSC_num_1_MDSC.pdf (tainstruments.com)]

Modulovaný signál






Sample: Quenched PET
Size: 10.1000 mg
Method: MDSC.424/40@4
Comment: MDSC..424/40@4 (Heat Only)
DSC
Figure 4
Heat Flow Rate at the Lowest Heating Rate of 0C/min
Modulated Heat Flow Rate
Heat Flow Rate at the Highest Heating Rate of 8C/min
Modulated Heating Rate
Modulated Heat Flow (mW)
Deriv. Modulated Temperature (°C/min)
4
0
-4
-8
-12
40
32
24
16
8
0
0
50
100
150
200
250
300
Exo Up
Temperature (°C)

Applying simultaneous heating rates (linear and modulated) provides further information on sample heat capacity or structure. The equation that describes the heat flow signal from a DSC or MDSC® experiment shows the benefit of this technique.

$$\frac{dH}{dt} = Cp\frac{dT}{dt} + f(T, t)$$

Where:

$\frac{dH}{dt}$ is the Total Heat Flow due to the underlying or linear heating rate. It is equivalent to standard DSC at the same average heating rate

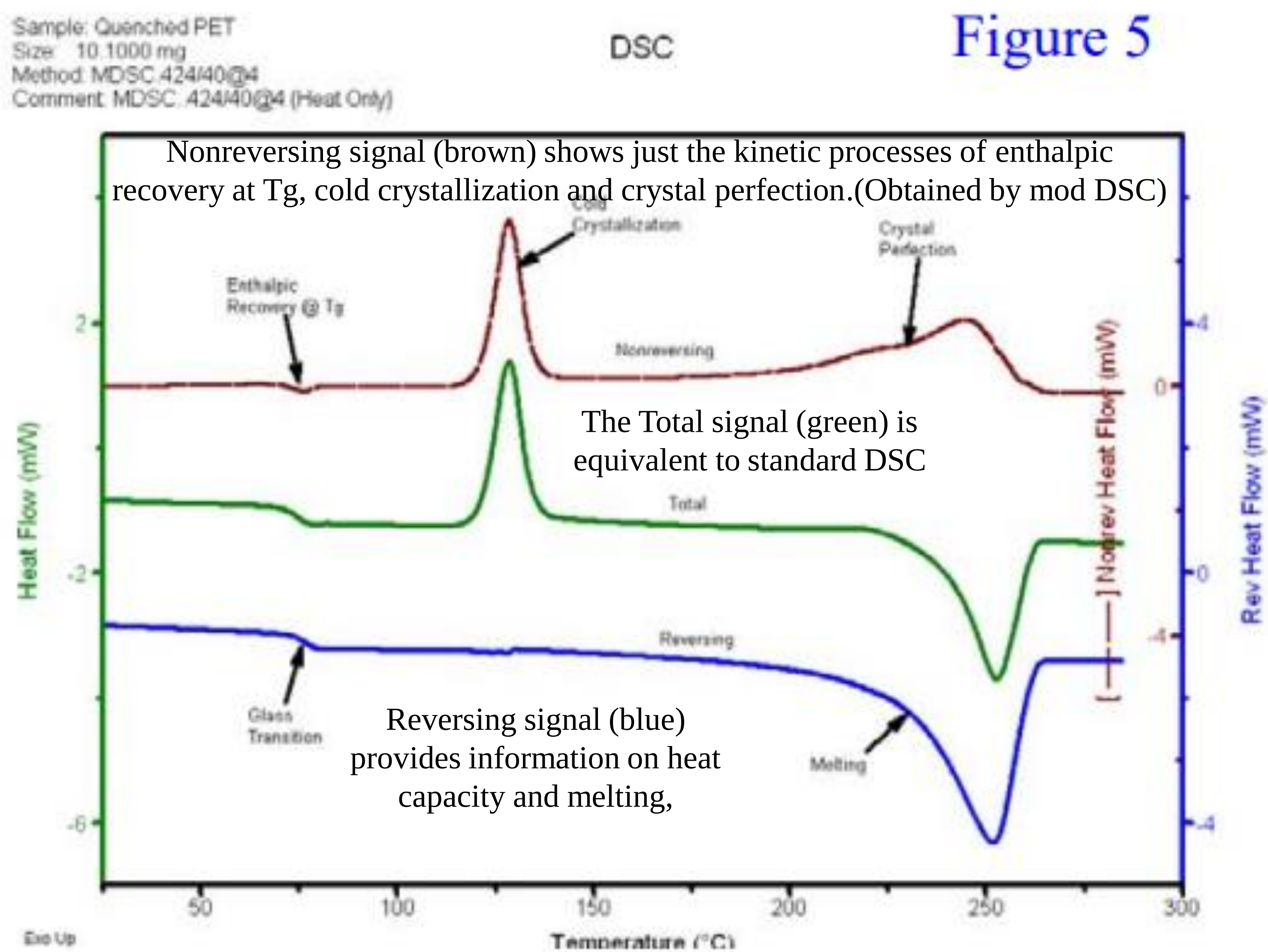
Cp is the Heat Capacity Component of the Total heat flow and is calculated from just the heat flow that responds to the modulated heating rate

$\frac{dT}{dt}$ is the measured heating rate, which has both a linear and sinusoidal (modulated) component

$f(T,t)$ is the Kinetic Component of the Total heat flow and is calculated from the difference between the Total signal and Heat Capacity Component.

$Cp\frac{dT}{dt}$ is the Reversing Heat Flow Component of the Total Heat Flow

Figure 5

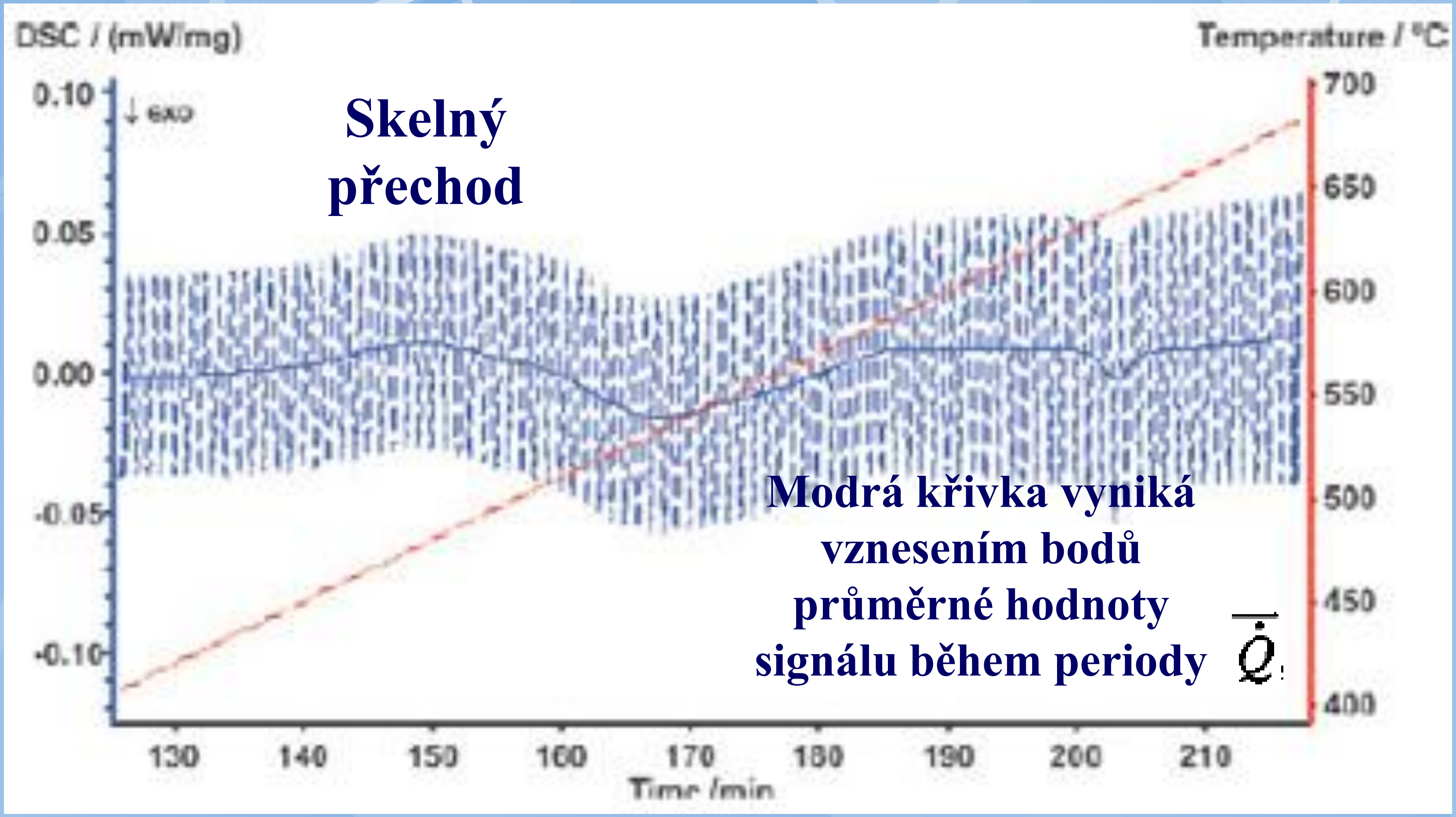


Nonreversing signal (brown) shows just the kinetic processes of enthalpic recovery at Tg, cold crystallization and crystal perfection.(Obtained by mod DSC)

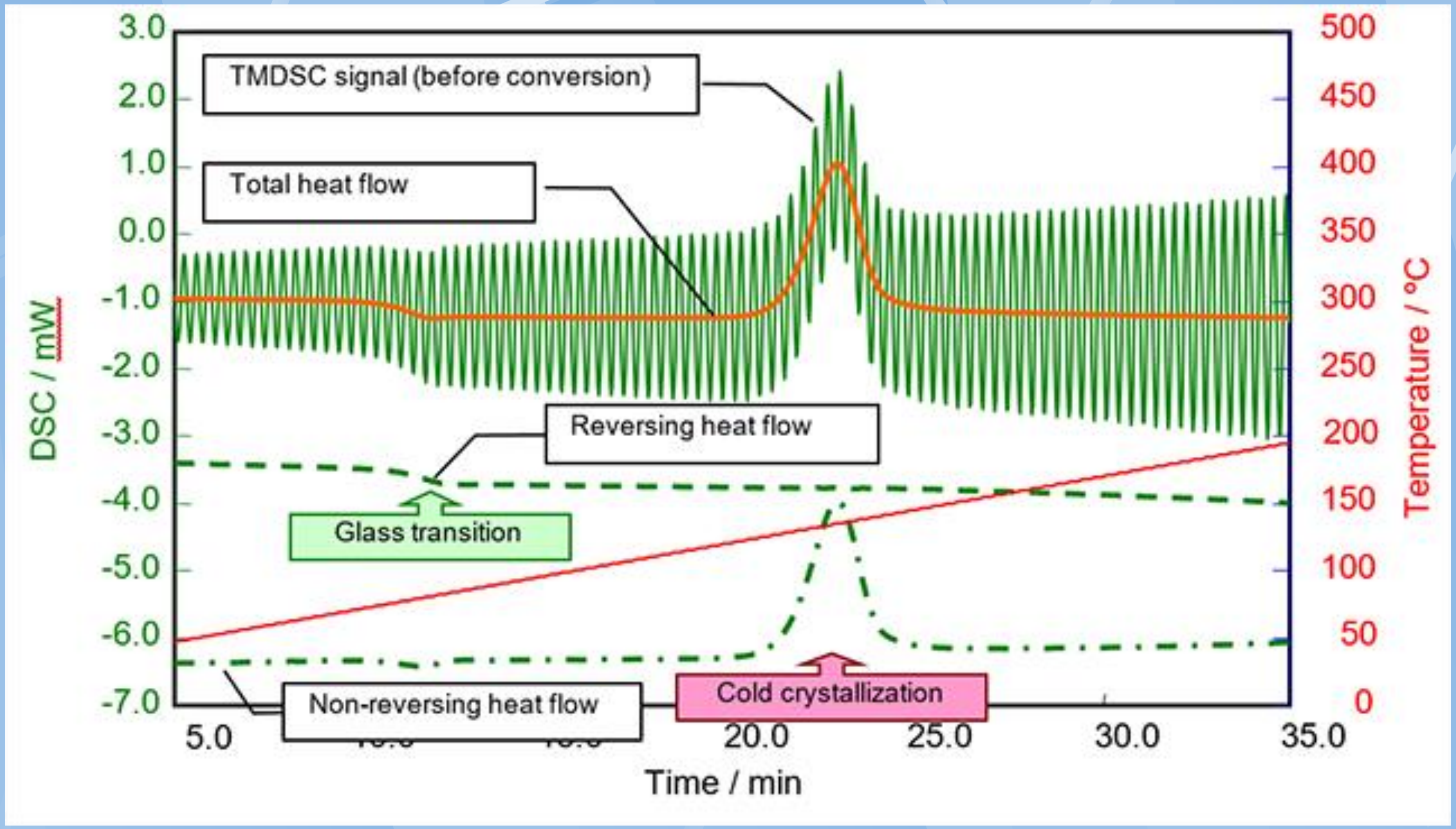
The Total signal (green) is equivalent to standard DSC

Reversing signal (blue) provides information on heat capacity and melting,

Nezpracovaný signál tmDSC



TM-DSC measurement of a glass sample, carried out with an STA 449 F1 Jupiter® system in synthetic air at a heating rate of 3 K/min, for a period of 60 s and with an amplitude of 0.5 K



[Temperature Modulated DSC | Thermal Analysis | Hitachi High-Tech (hitachi-hightech.com)]

Zpracování tmDSC signálu pro quasi isotermní tmDSC

$\overline{\dot{Q}}_s$ průměrná hodnota signálu během periody (odpovídá celkovému signálu klasické DSC)

$$\begin{cases} T_s = \beta t + \mathrm{Re}[\tilde{T}_s e^{i(\omega t+\varepsilon)}] \\ \dot{Q} = \overline{\dot{Q}} + \mathrm{Re}[\tilde{\dot{Q}} e^{i(\omega t+\delta)}] \end{cases}$$

$$\tilde{\dot{Q}} e^{i(\omega t+\delta)} = -C_0 e^{-i\varphi} \frac{d}{dt} \tilde{T}_s e^{i(\omega t+\varepsilon)}$$

$$\Rightarrow C_0 = \frac{\tilde{\dot{Q}}}{\omega \tilde{T}_s} \quad \text{and} \quad \varphi = \varepsilon - \delta - \frac{\pi}{2}$$

$\tilde{\dot{Q}}$ …amplituda tmDSC isgnálu

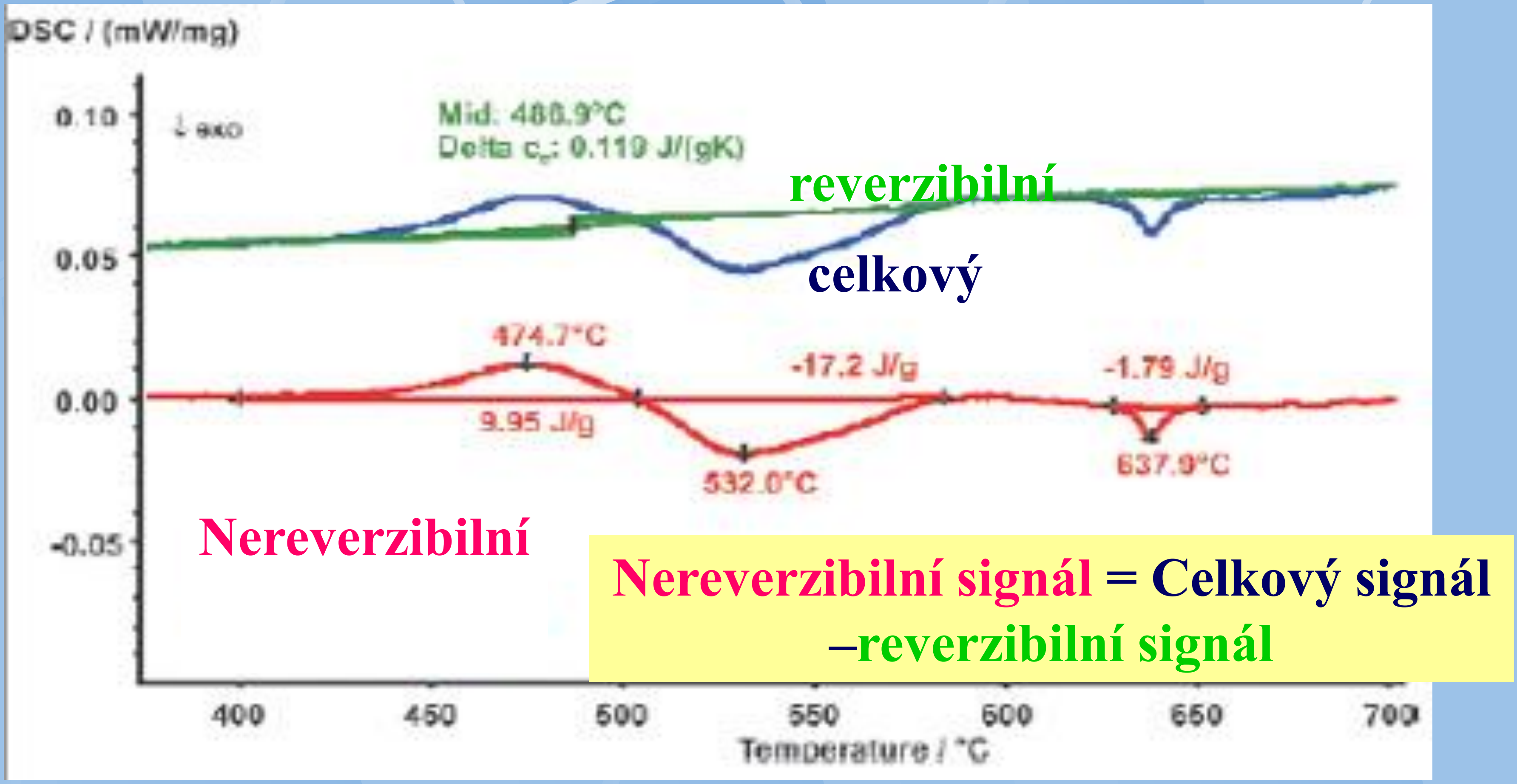
$\tilde{T}_s$ …amplituda Ts teploty vzorku

tmDSC určí: $C_0\, e^{-i\varphi}$

Kde C_o je modul a φ fázový úhel

C_0 je reverzibilní signál tmDSC

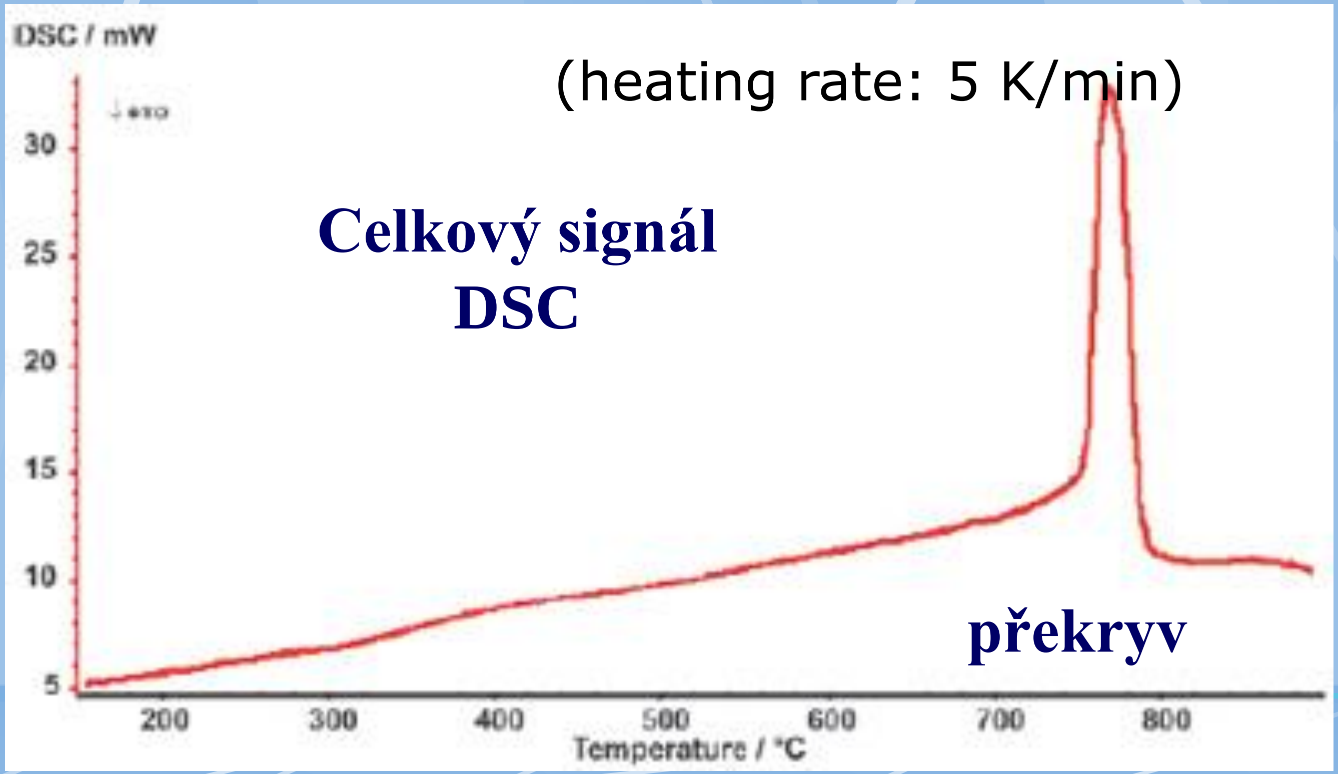
Separace nereverzibilního a reverzibilníhio signálu



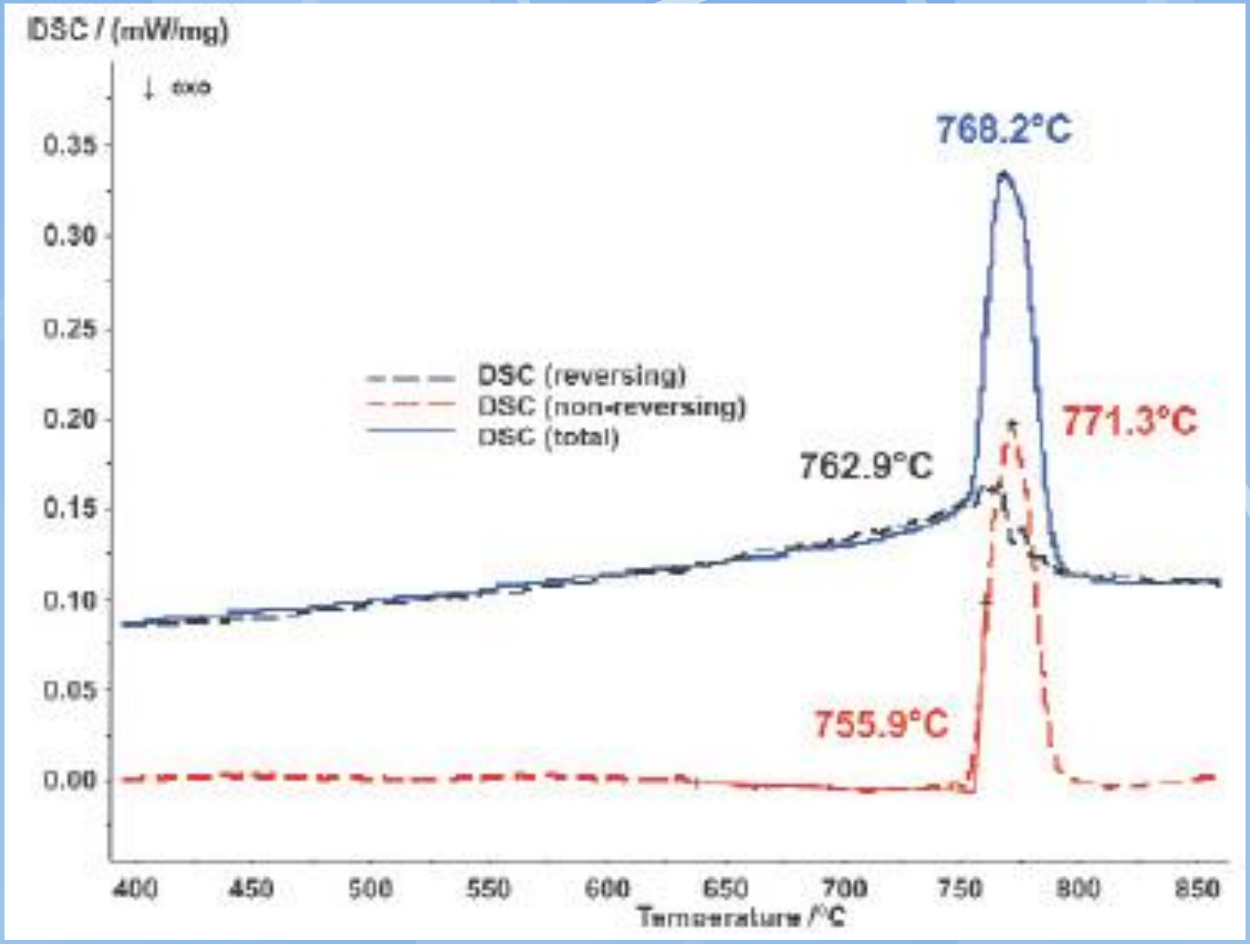
Measurement curve of fig. 2 split into the reversing and the non-reversing signal. The glass transition is clearly visible in the reversing signal (green curve); the non-reversing signal (red curve) shows the relaxation as well as two crystallization effects. The blue curve is the total heat flow curve, equivalent with the curve of a conventional DSC instrument.

Aplikace: Běžné DSC měření oceli

Překrývá se fázová přeměna (alfa-gama (tj. FP 1.druhu), ireverzibilní děj (např. ploch zrn) a magnetická přeměna ($T_{C,}$, FP 2.druhu (tj. reverzibilní děj) při 700-800stC v závislosti na obsahu legur a uhlíku.



Separace signálu



Tc=762,9ºC

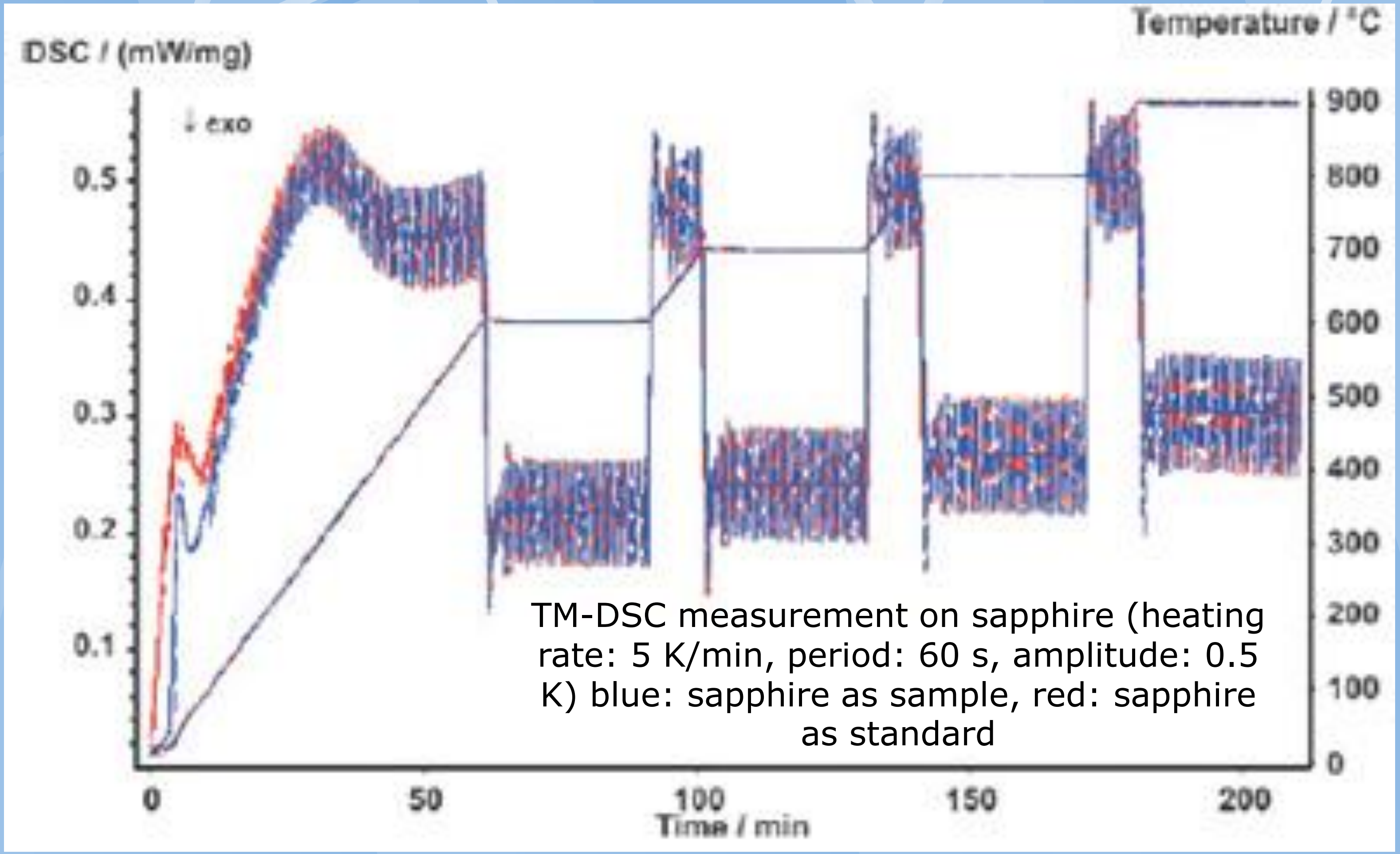
Alfa –gama:

Onset: 755,9 ºC

End: 771,3 ºC

TM-DSC measurement on steel (heating rate: 5 K/min, period: 60 s, amplitude: 0.5 K) blue: total heat flow, red: non-reversing curve, black: reversing curve

Získávaný signál: quasi isotermická tmDSC

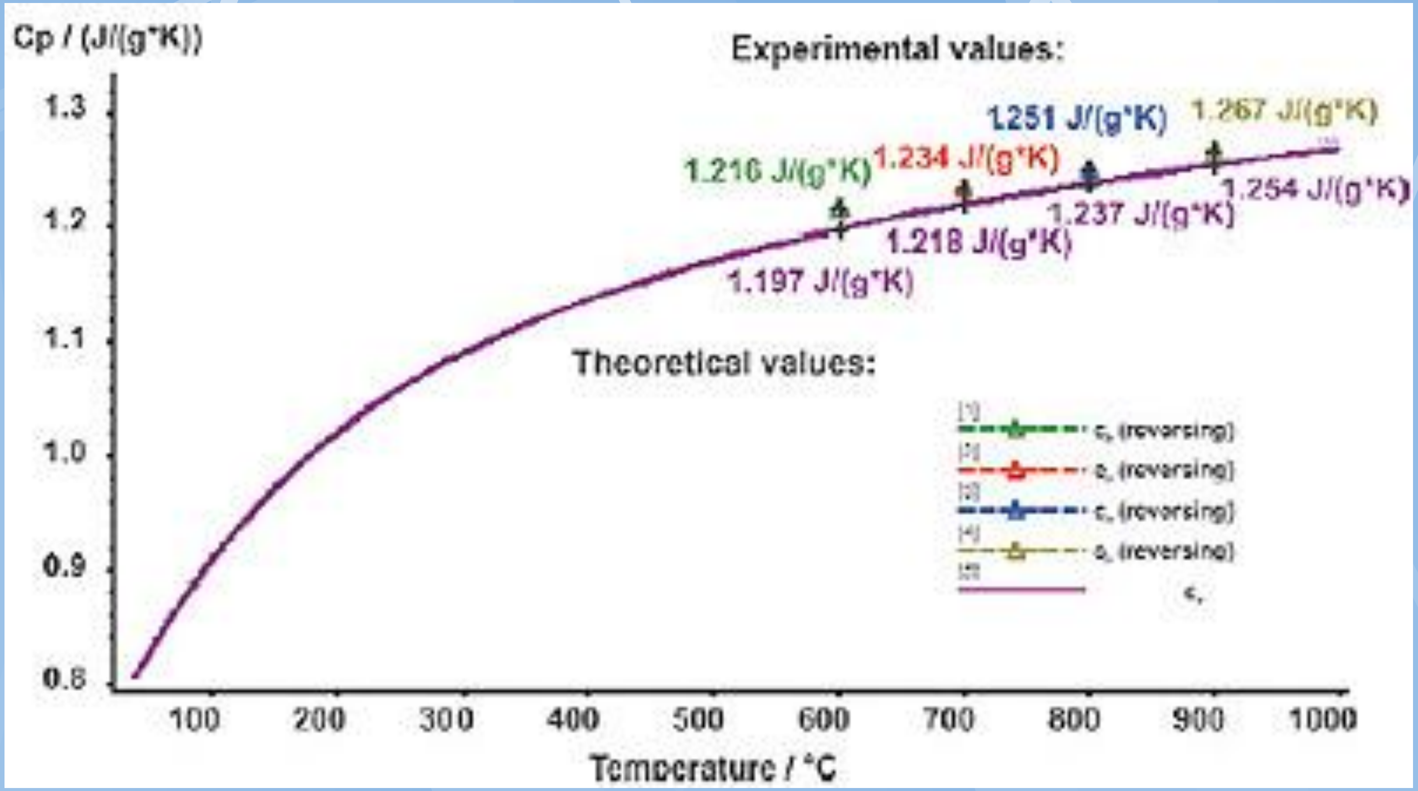


TM-DSC measurement on sapphire (heating rate: 5 K/min, period: 60 s, amplitude: 0.5 K) blue: sapphire as sample, red: sapphire as standard

Ustálení pece

Isotermické skoky s modulací

Výsledek měření Cp (quasi isotermní měření)



Specific heat determination on sapphire - comparison between experimental (colored symbols) and theoretical data (violet curve)

Diskuze

Detaily tmDSC:
http://www.anasys.co.uk/library/dsc4.htm

- http://www.anasys.co.uk/library/dsc5.htm
- http://www.americanlaboratory.com/914-Application-Notes/18836-A-Multifrequency-Temperature-Modulated-Technique-For-DSC/
- http://www.azom.com/article.aspx?ArticleID=4982