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MATERIALS

Calorimetry on pure substances and complex non-equilibrium Al-systems

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- *Motivation*
- *Differential Scanning Calorimetry on Aluminium alloys*
- *DSC Step Scan method for cp measurement*

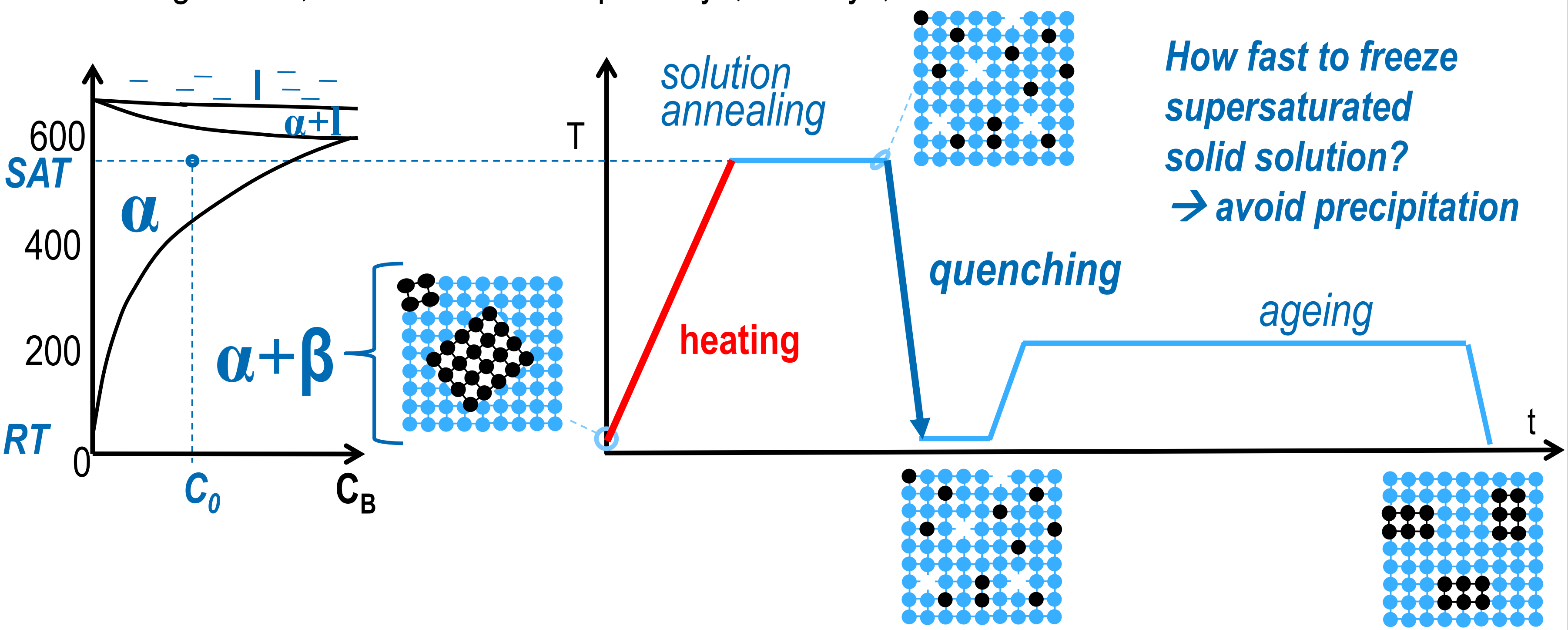
heat treatment of metallic materials

basic scheme applies for several materials

e. g. steels, Ni- & Co based superalloys, Al alloys, …

How slow to dissolve everything?
→ full solution

How fast to freeze supersaturated solid solution?
→ avoid precipitation



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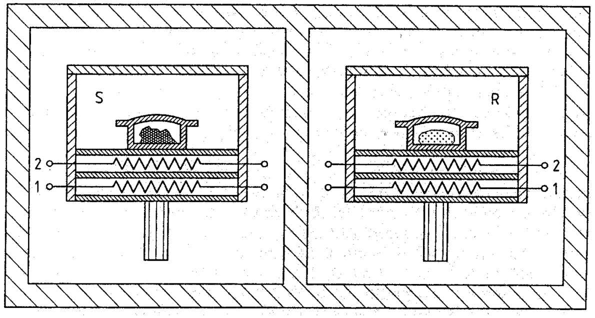
Differential Scanning Calorimetry (DSC)

measurement of (tiny) heat

- 2 identical micro furnaces in symmetric system
- PC controlled temperature programs: heating/ cooling
- regulation: equal temperature
- difference in heating power or heat flow measured

G.HÖHNE, W. HEMMINGER, H.FLAMMERSHEIM:
Differential Scanning Calorimetry, *SPRINGER*



S: sample furnace; R: reference furnace (equal S), 1heating wire, 2 Thermopile; measuring systems – separately – in ambience of const. temperature

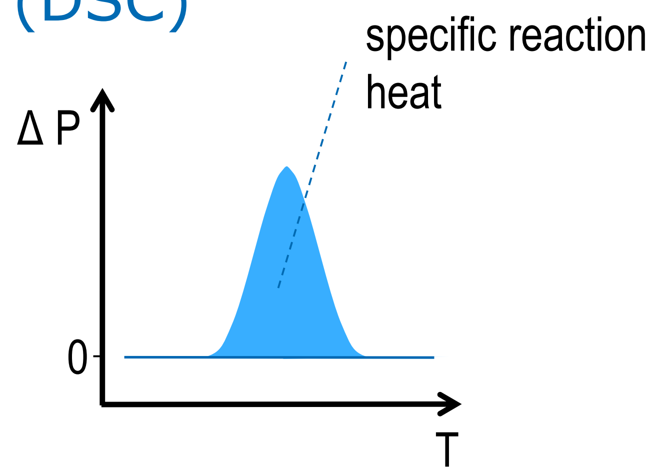
Differential Scanning Calorimetry (DSC)

functional principle

ideal:

heating/ cooling empty system: signal = 0

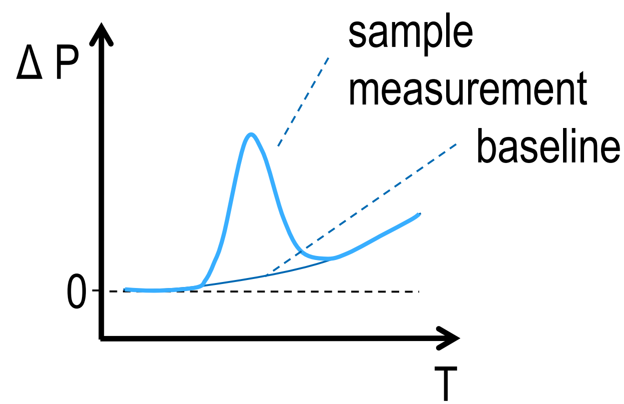
thermal reaction in sample furnace: Signal ≠ 0



real:

certain asymmetry: device depending bending

correct: subtract baseline from sample measurement



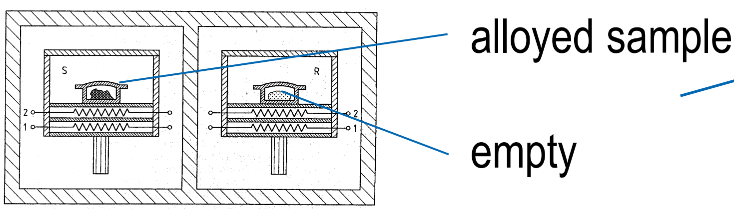
Preliminary tests Al alloys

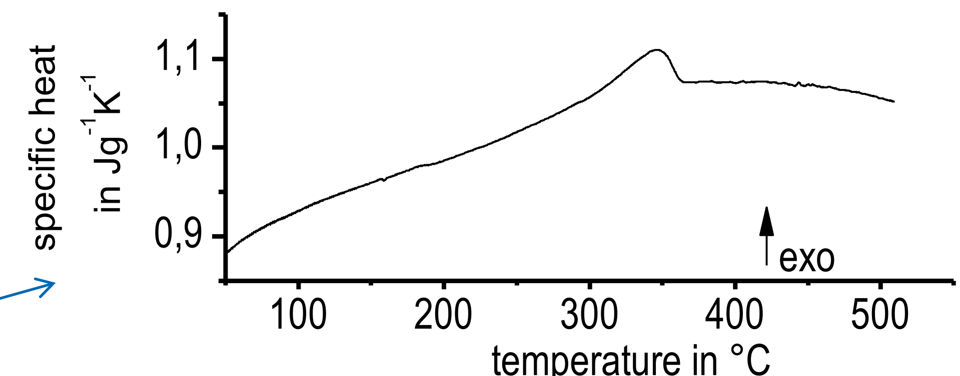
How to measure precipitation heat – Cp or excess-Cp?

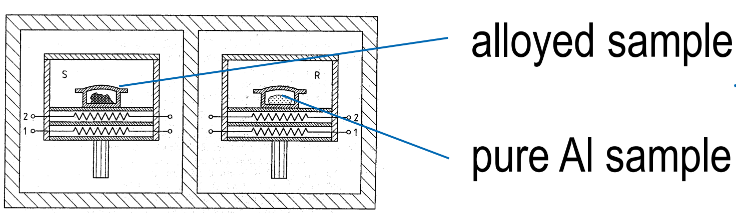
cooling EN AW-6005A , 50 K/min

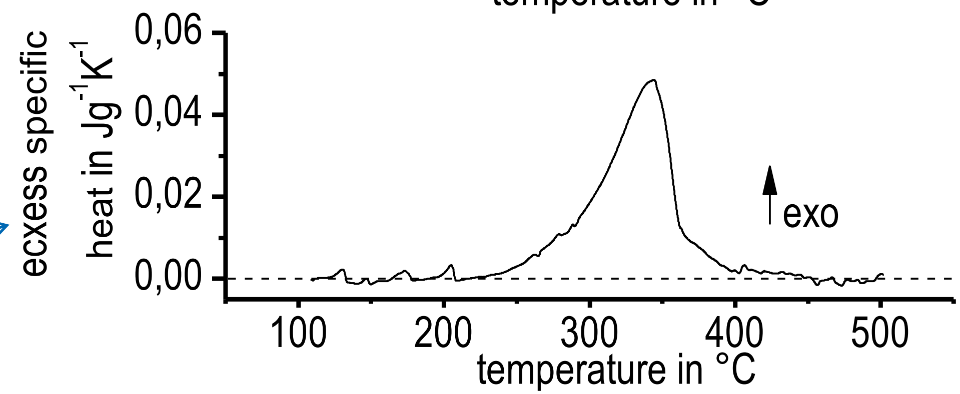
Perkin-Elmer Pyris 1

after: 540 °C 20 min









Preliminary tests Al alloys

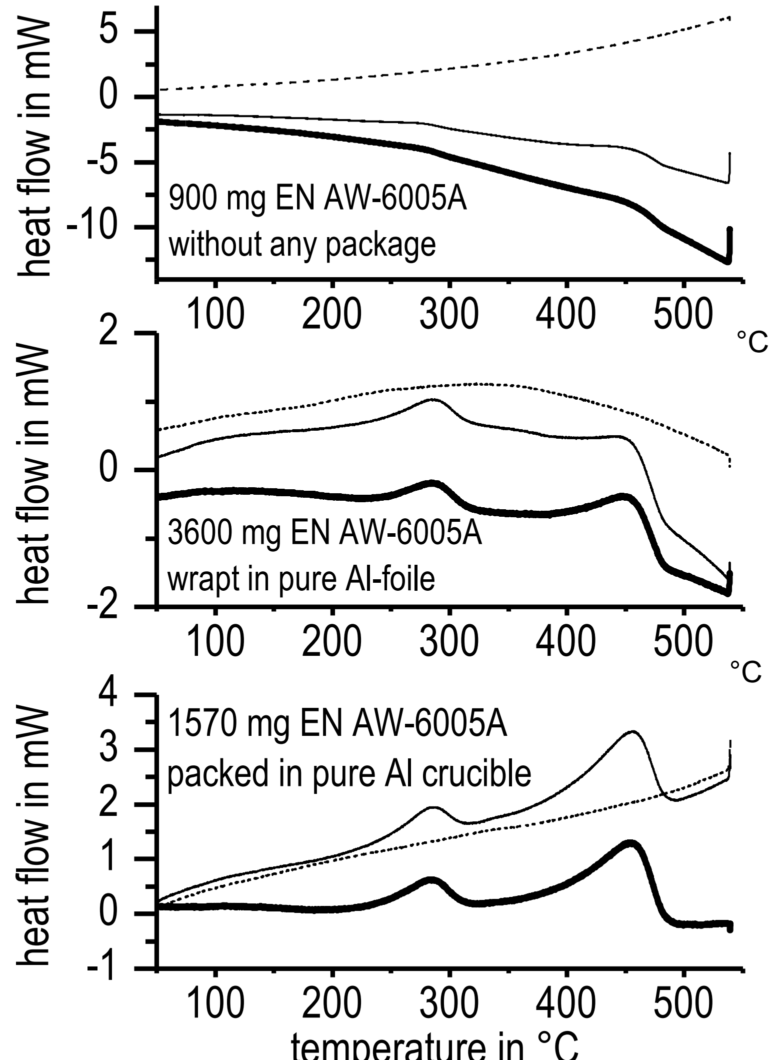
Obligatory sample package!

- important role of radiation losses → baseline stability
- samples change surface color: bright → dark grey

  radiation effect changing → bending
- bending reduction → sample package!

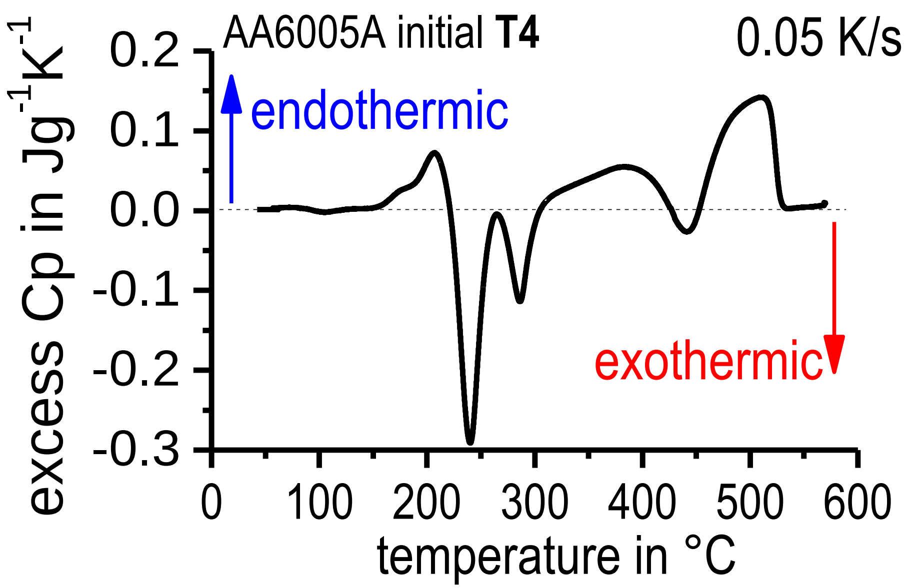
Setaram 121 DSC
cooling with 0.5 K/min after
solution annealing: 540°C 20 min

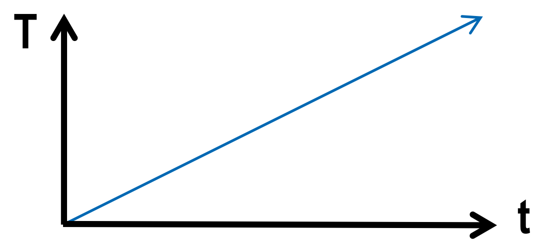
——— Sample-measurement
- - - - Baseline-measurement
——— subtraction of sample- & baseline-measurement



DSC measures heat effects

sample compared with inert reference sample





Challenge

Very large scale of technically & physically interesting heating & cooling rates!

e.g. one cooling method – different component dimensions

MMG GmbH

auto-lexikon.de

weloe.de

fi-sch.de

1E-4 1E-3 0,01 0,1 1 10 100 1000 10000 100000

cooling rate in K/s

range depends on physical requirements alloy, heating/cooling procedure, dimensions

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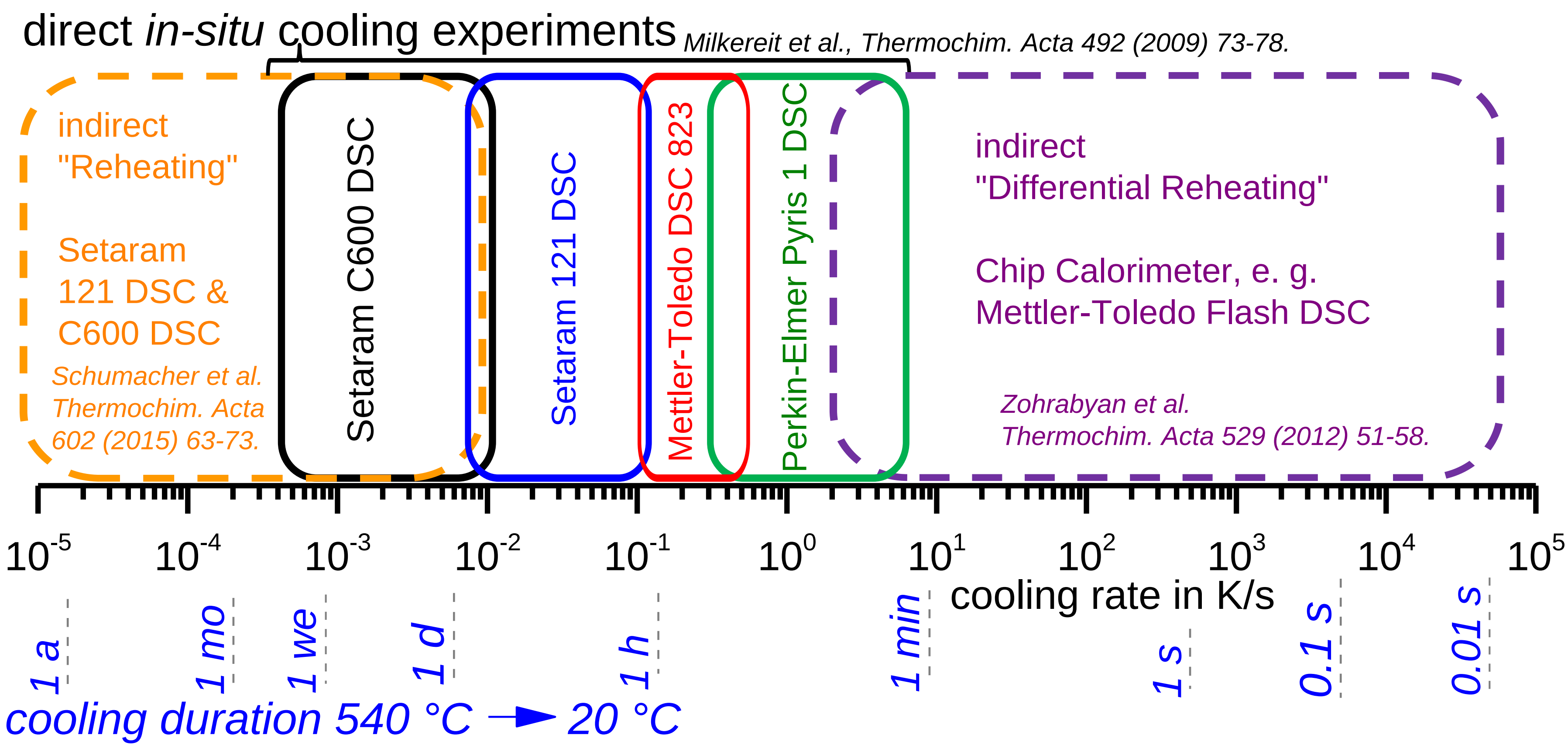
How to cover all relevant rates?

Use different DSC types and methods

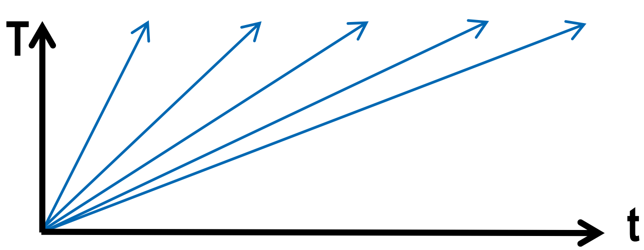


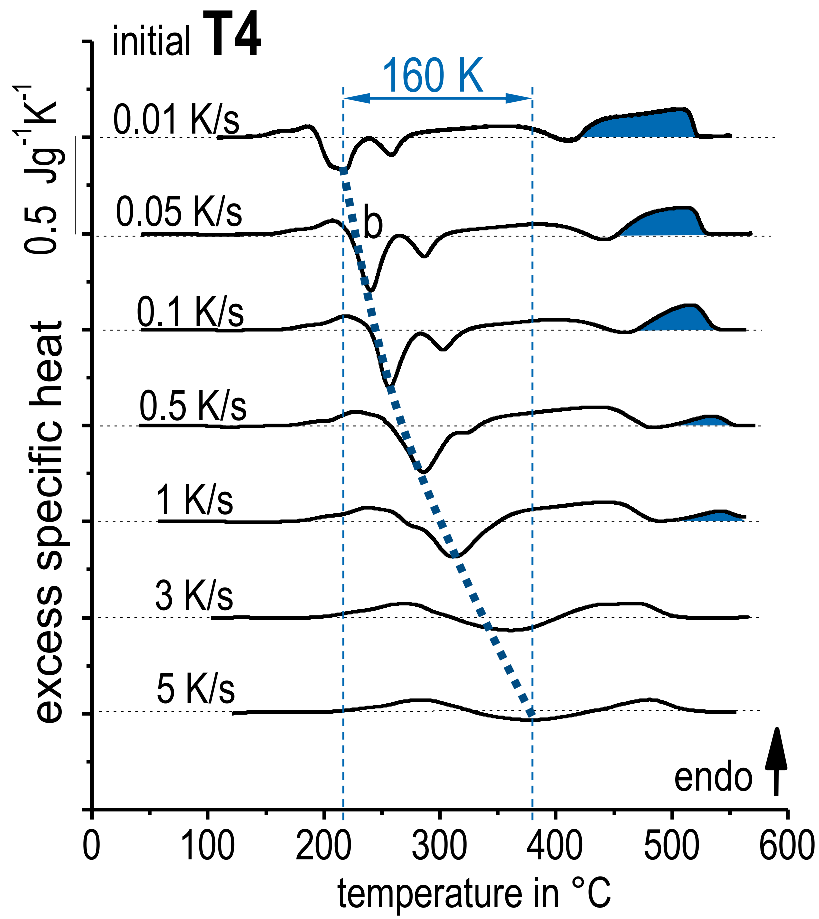
J. Osten et al.. Dissolution and Precipitation Behaviour during Continuous Heating of Al–Mg–Si Alloys in a Wide Range of Heating Rates. Materials 2015, 8, 2830-2848. DOI: 10.3390/ma8052830

Continuous heating DSC AA6005A to 580 °C

0.01 – 5 K/s

- suppression of reactions with increasing rate
- serious peak shift, e. g. peak b:
  - observed ΔT: 160 K
  - thermal lag ≈ 10 K





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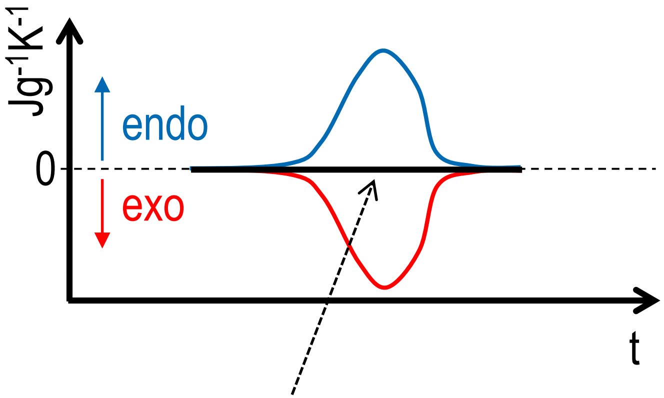
challenges for interpretation of DSC heating curves

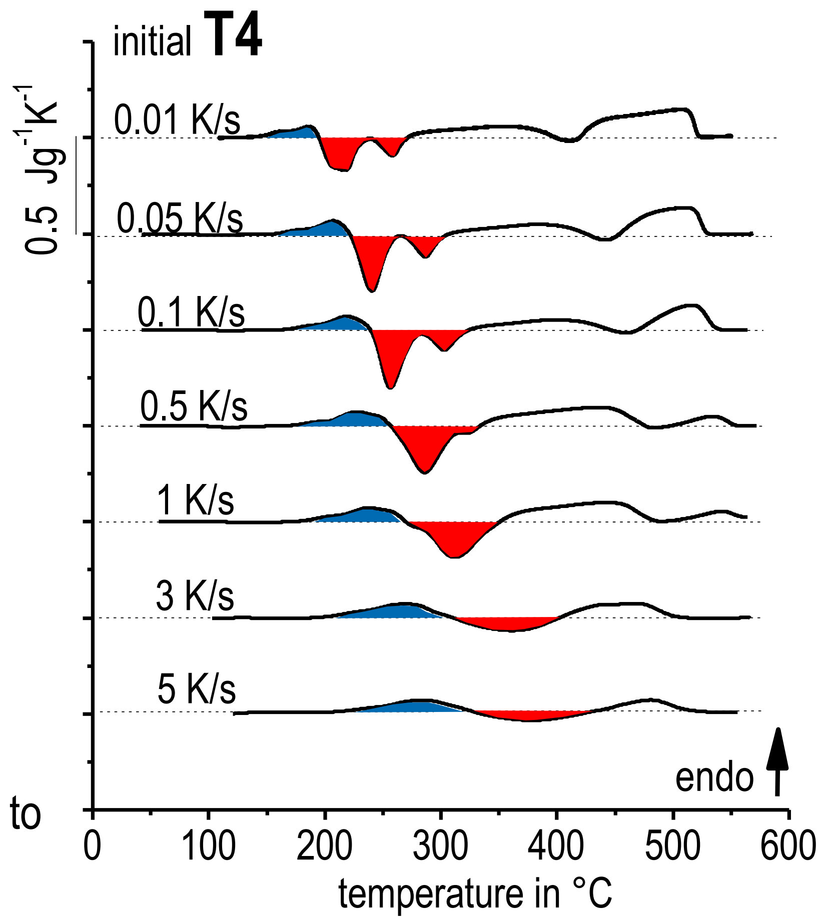
serious overlapping several reactions



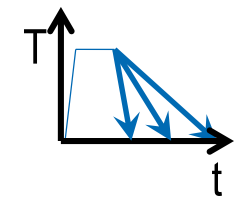
DSC measures sum signal!

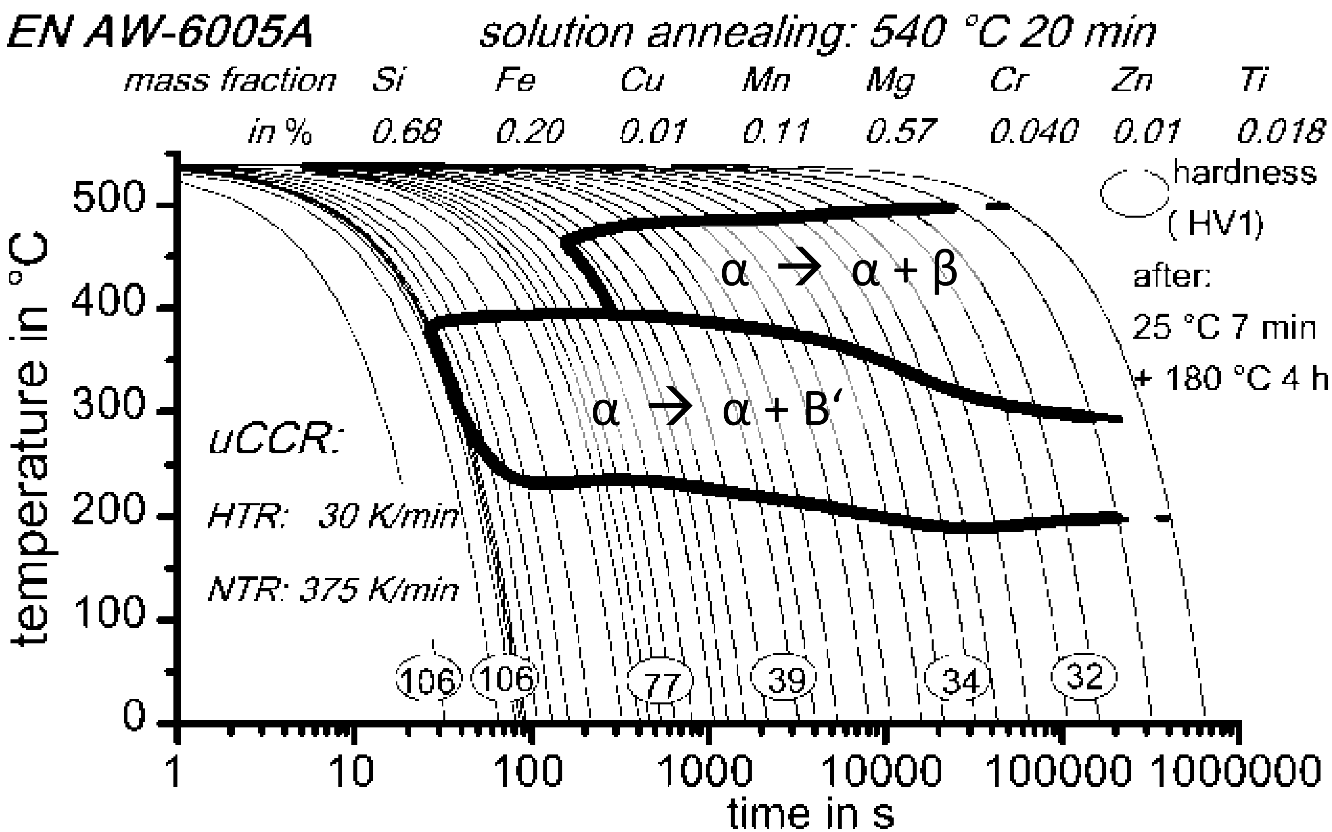
sum might be zero...

→ separation of overlapped reactions problem to solve in future

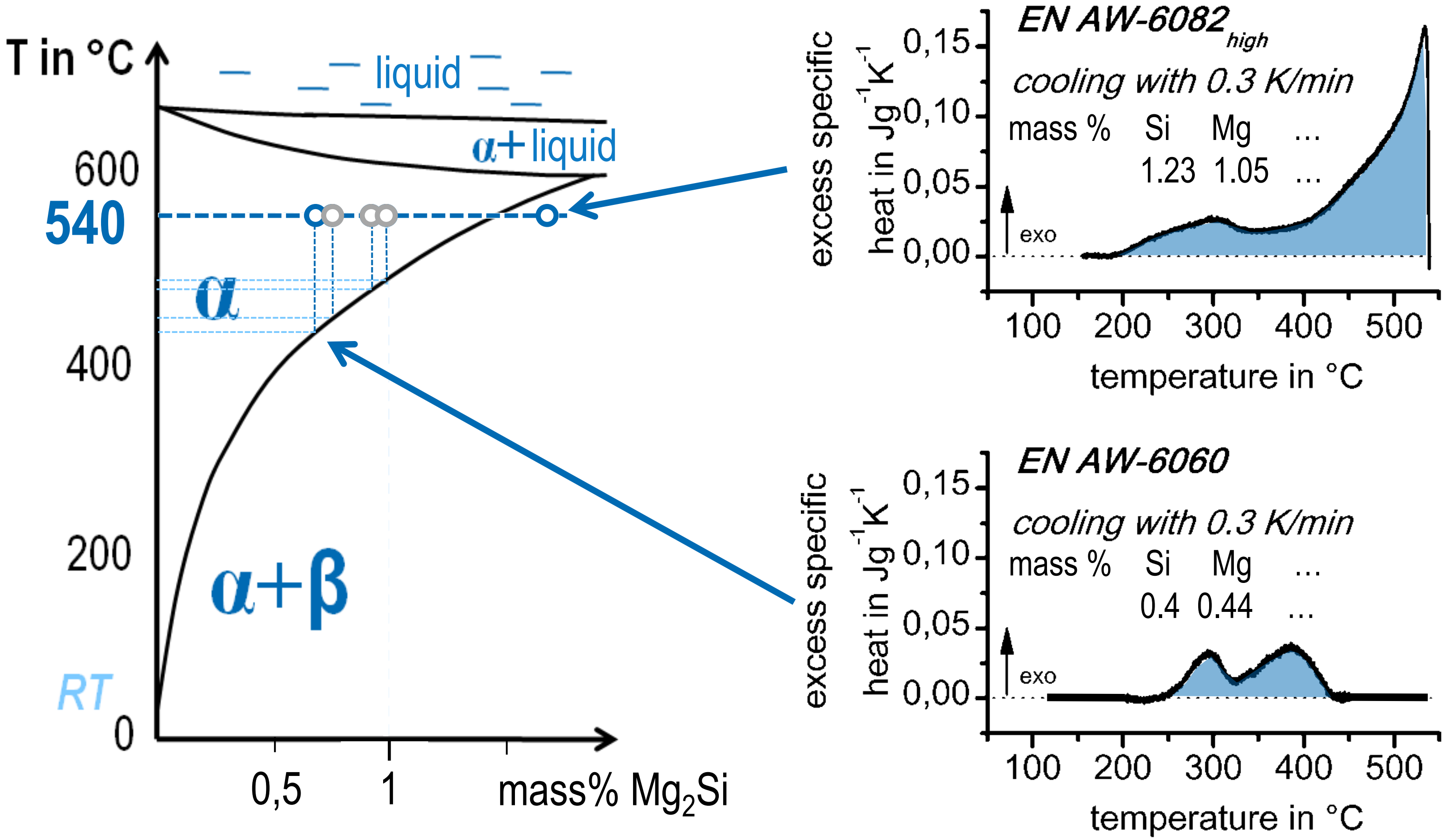


Continuous cooling precipitation diagrams





precipitation start temperature

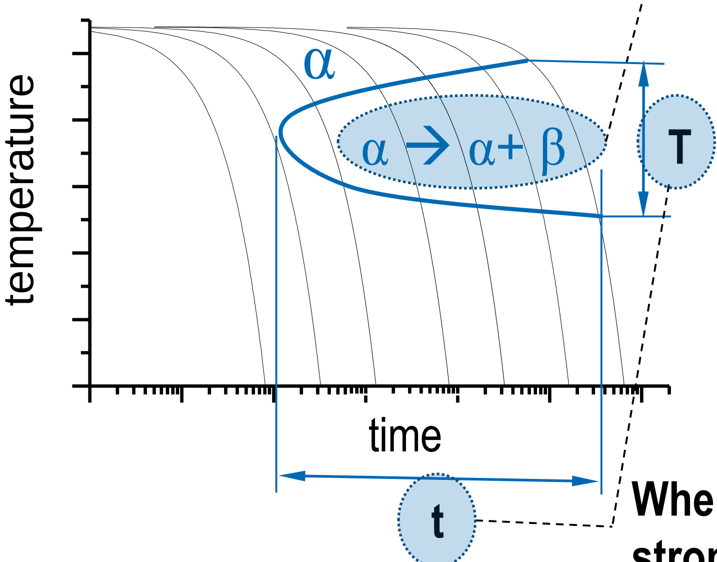


Method

Which reactions occur when and how intensive?

Milkereit, B., et al. (2012). "Continuous cooling precipitation diagrams of Al-Mg-Si alloys." Materials Science & Engineering A 550: 87-96. DOI: 10.1016/j.msea.2012.04.033

Which?

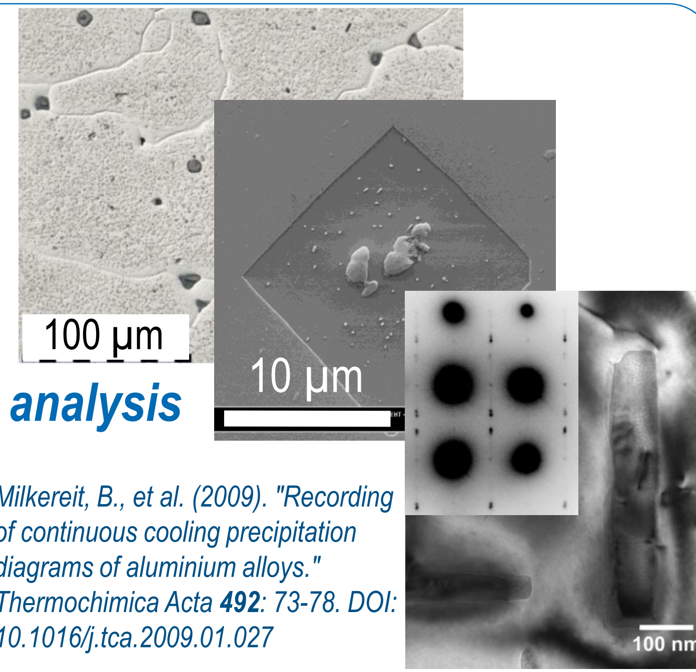


When & how strong?

Structure analysis

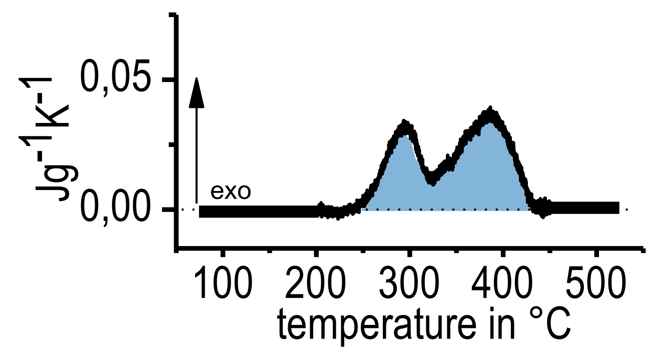
CCP-diagrams

Differential Scanning Calorimetry



*Milkereit, B., et al. (2009). "Recording of continuous cooling precipitation diagrams of aluminium alloys." Thermochimica Acta **492**: 73-78. DOI: 10.1016/j.tca.2009.01.027*

cooling of an aluminium alloy



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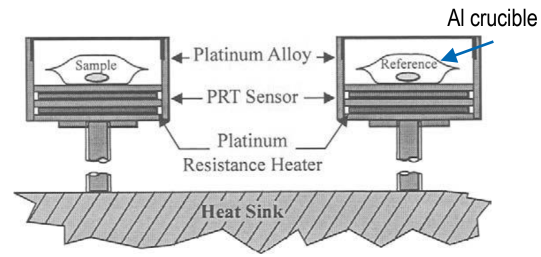
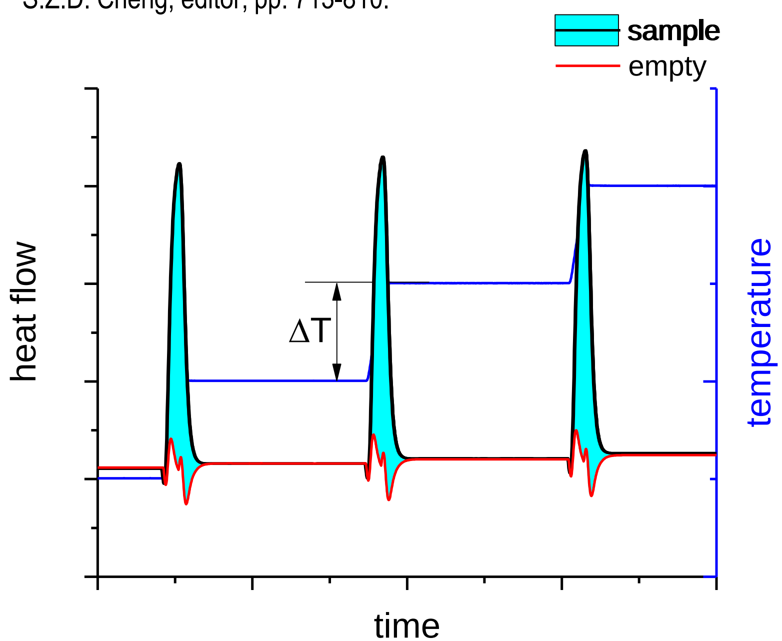
cp measurement with DSC

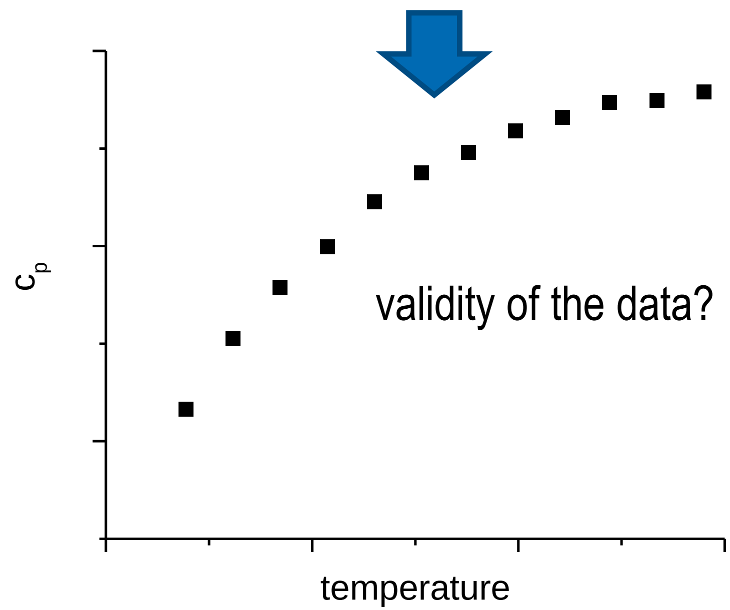


high accuracy through step scan method

C. Schick (2002): Temperature modulated differential scanning calorimetry (TMDSC)- basics and applications to polymers In: Handbook of Thermal Analysis and Calorimetry. Vol. 3: Applications to Polymers and Plastics S.Z.D. Cheng, editor, pp. 713-810.

$$\frac{\int \dot{Q}_{sample} - \dot{Q}_{empty}\,dt}{m\,\Delta T}$$

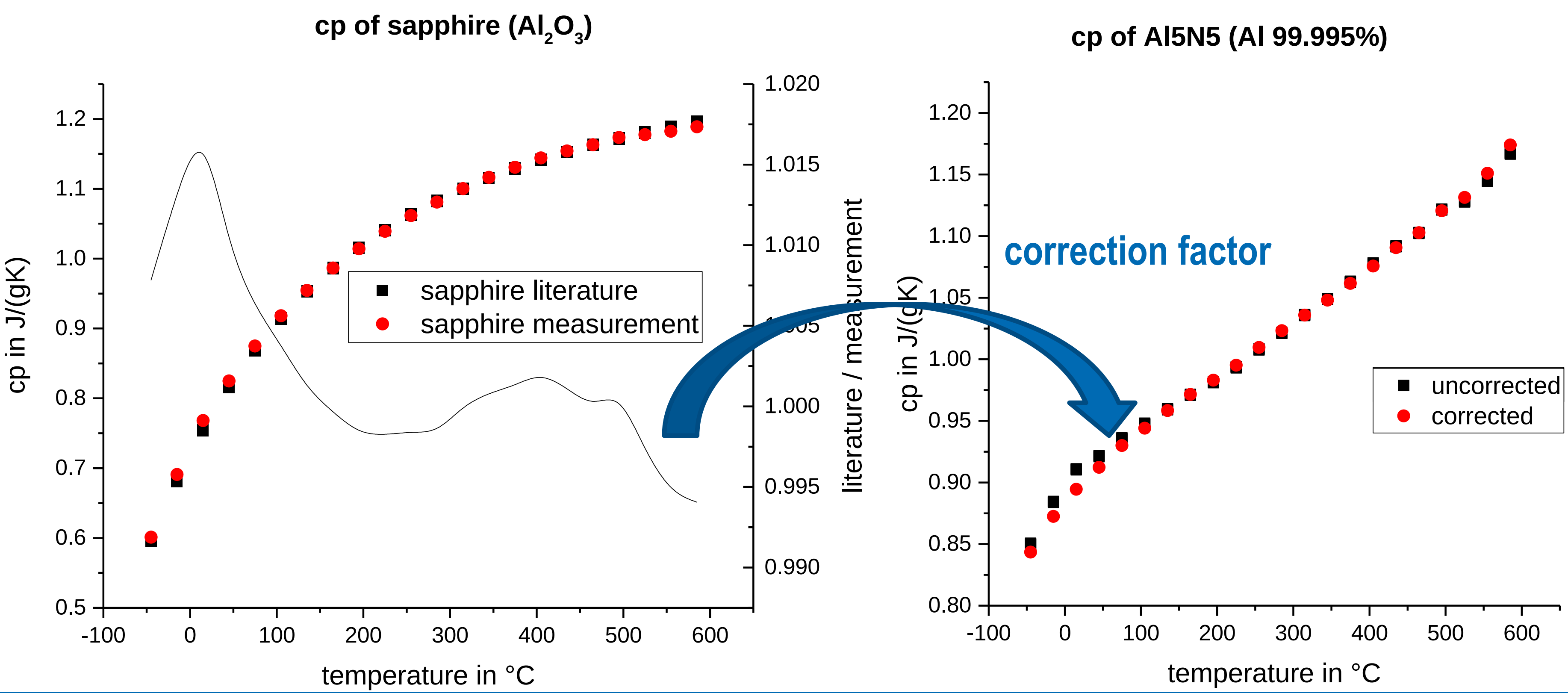




calibration with sapphire

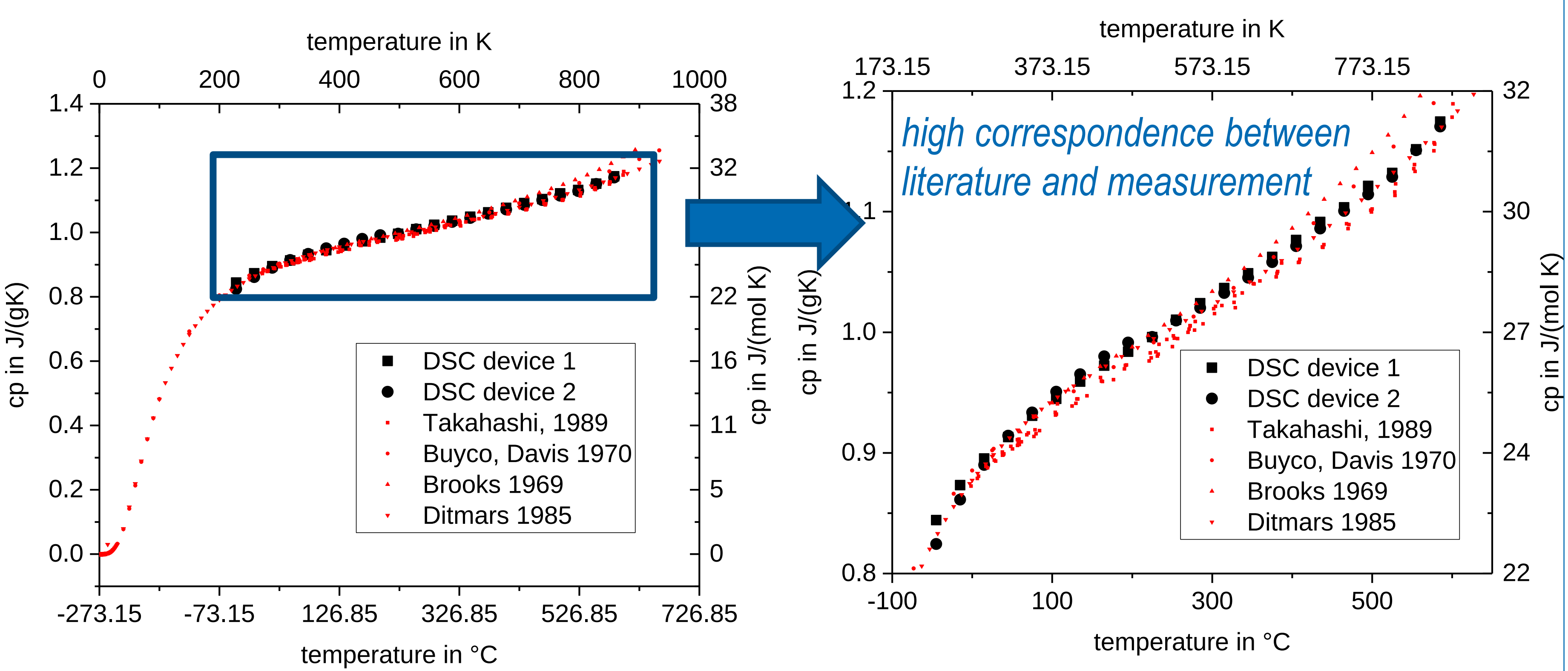
- well known cp of sapphire
- after each sample measurement

→ error correction



evaluating the data

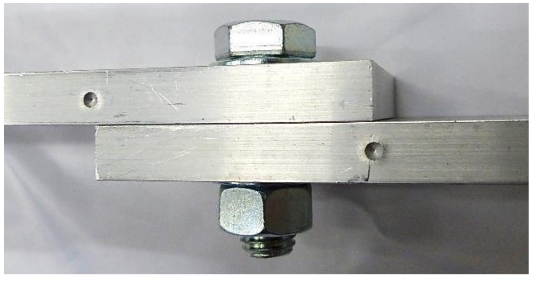
comparison cp of pure Al with different literature sources



step scan application on intermetallic phases

why important?

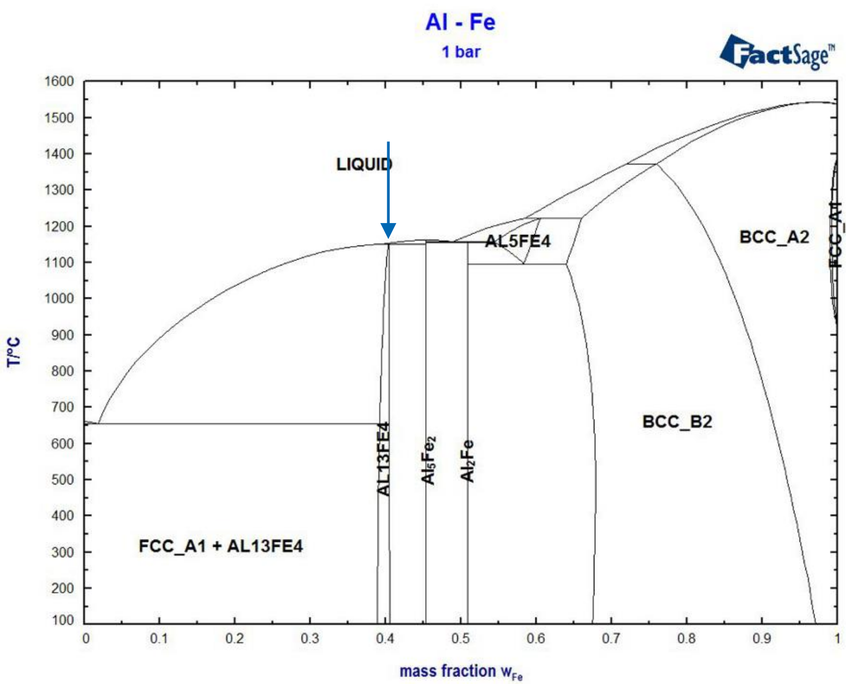
- aluminium alloys for long-term stable
  electrical aluminium connections (ALLEE)
  → large collaborative project (GTT, Hydro Aluminium, TU Dresden, RWTH Aachen)

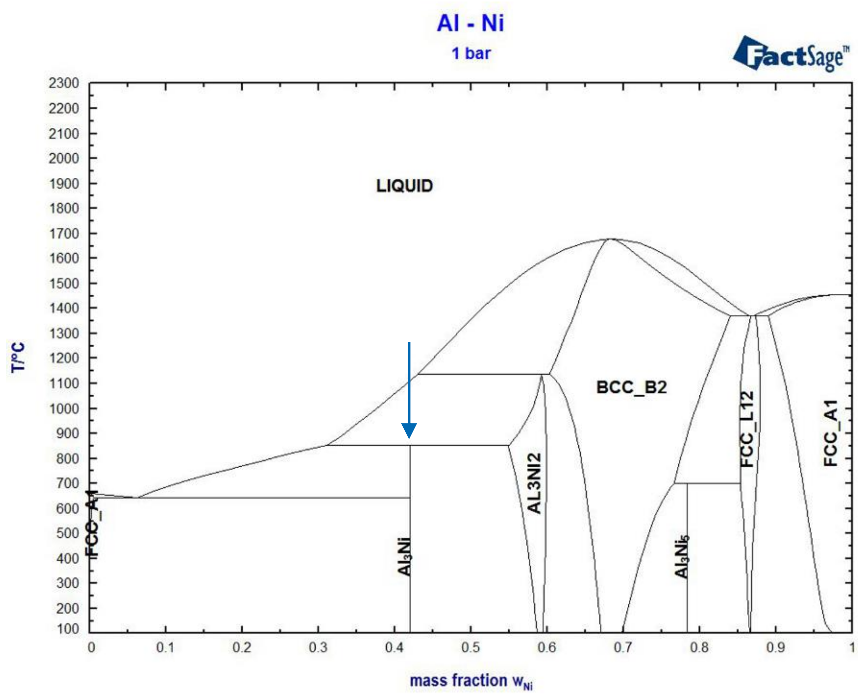


- **goal:**
  long-term stable intermetallic phases (e.g. Al3Zr, Al3Ni)
  also at elevated temperatures (140 °C)

- **challenge:**
  prediction (modelling) of precipitation and dissolution/growth
  investigation of Al alloy: sum cp of all phases ☹
- **solution:** *very difficult to produce!*
  investigation of **pure intermetallic phases** (Uni Jena, Germany) ☺

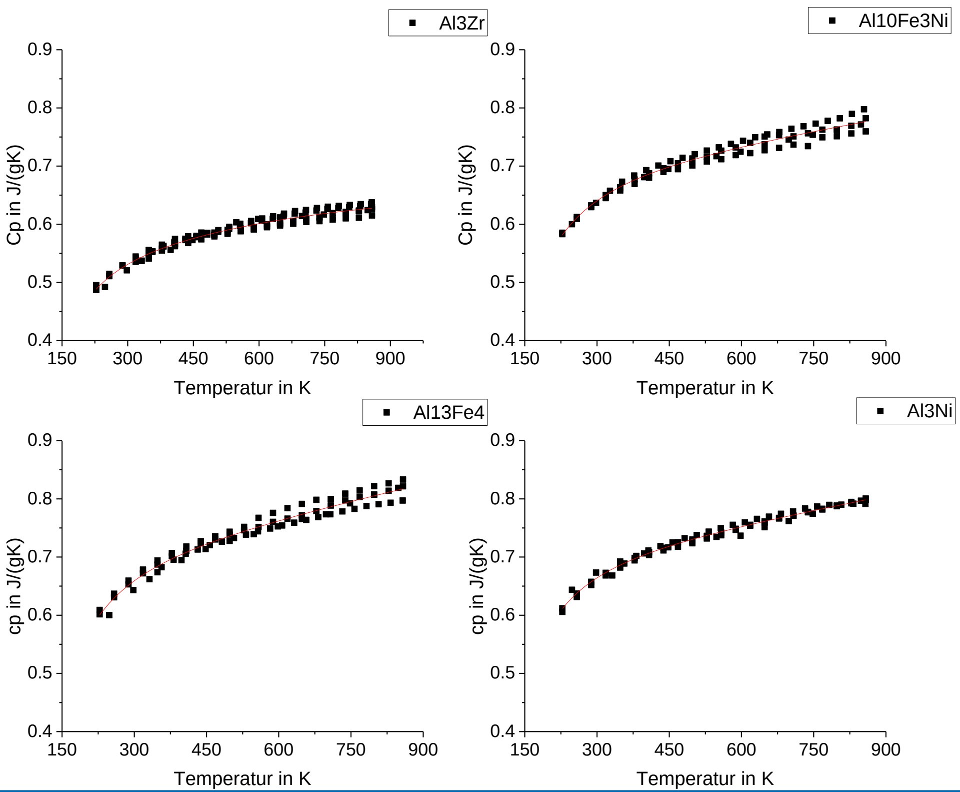
intermetallic phases

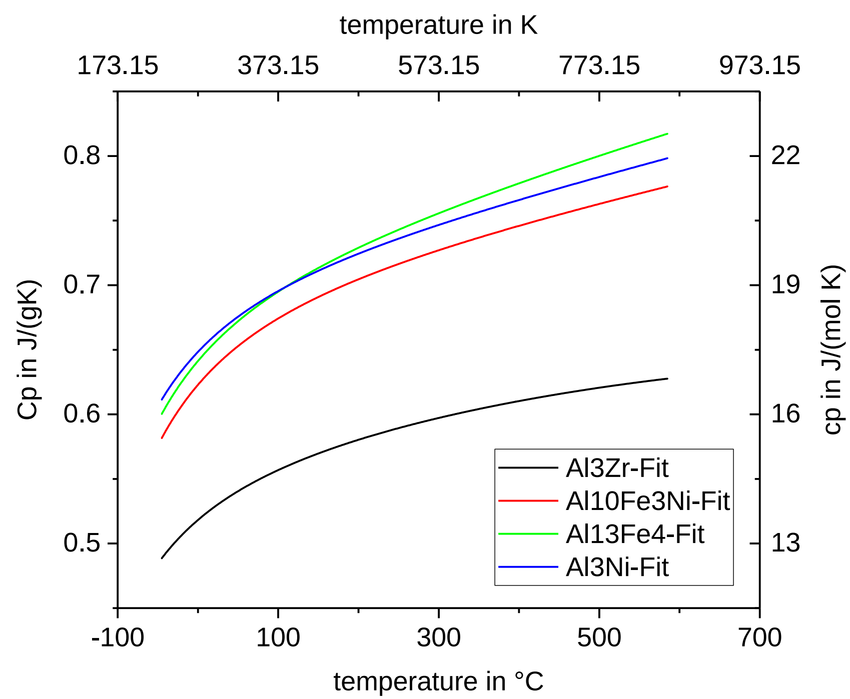




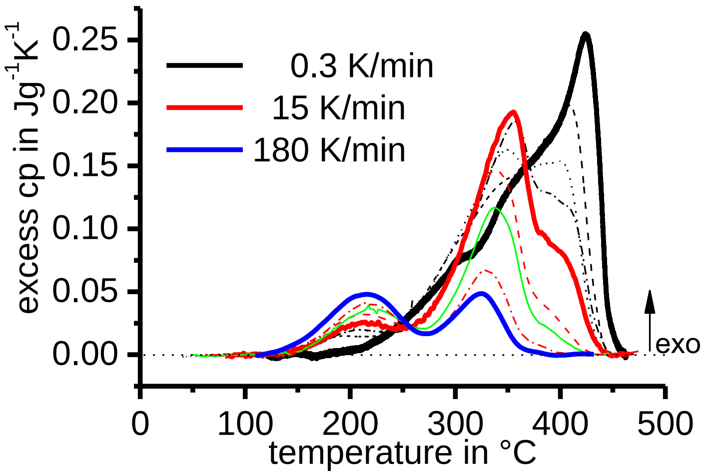
results

pure intermetallic phases Al3Zr, Al13Fe4, Al3Ni, Al10Fe3Ni





cooling of ***EN AW-7150*** *after 480 °C 1 h*



cooling ***EN AW-Al Zn8MgCu*** *from 470 °C*