ecoTRE VALENTE
TECNOLOGIE D'AVANGUARDIA

UNIVERSITÀ DEGLI STUDI DI TORINO
ALMA UNIVERSITAS TAURINENSIS

Collaboration in the field of precious alloys

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OUTLINE

- *Introduction*
- *Validation of the method*
- *Au-based alloy 2504*
- *Conclusions*

Annealing treatments in jewellery manufacturing

INTRODUCTION

Annealing

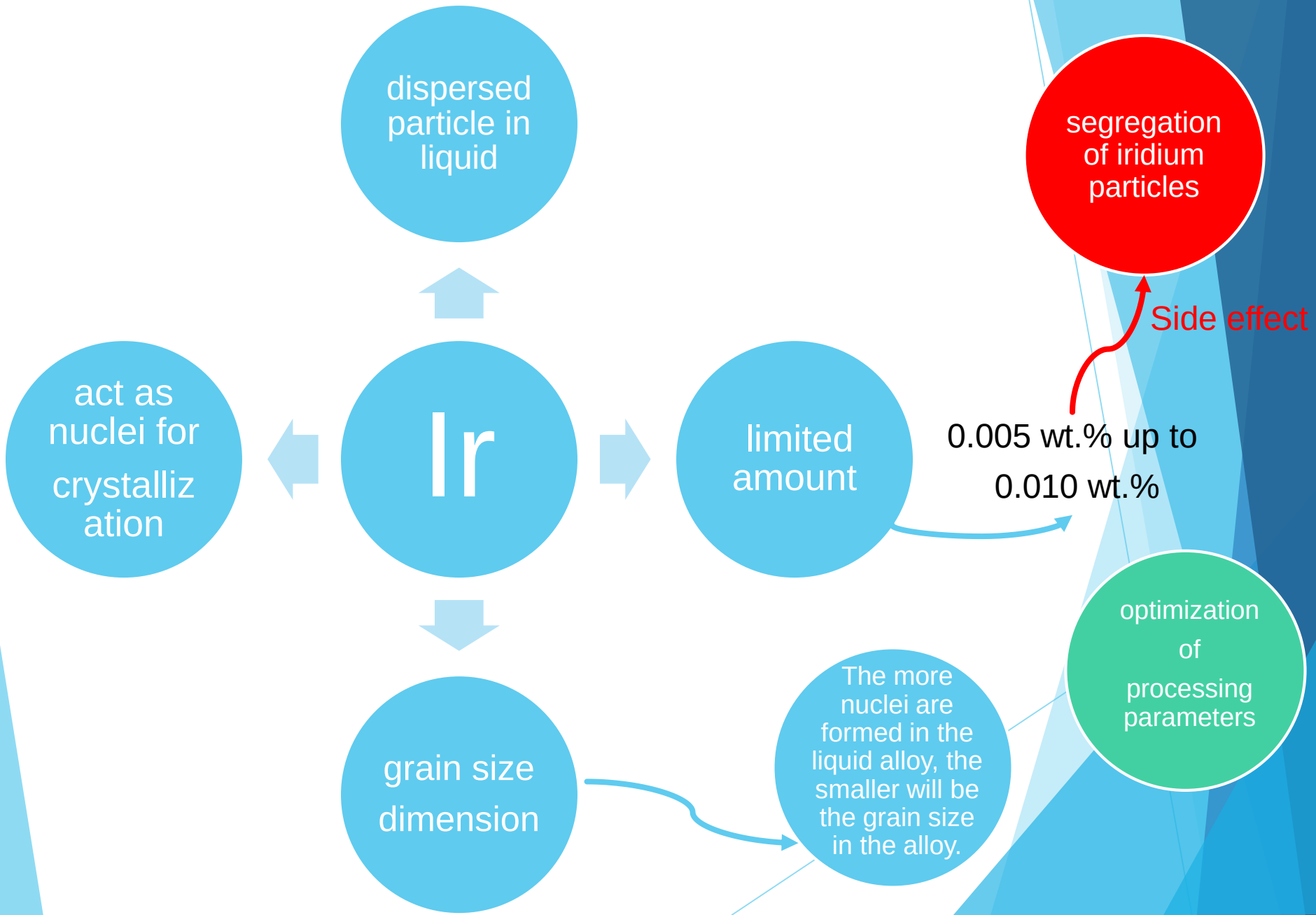
- restore ductility by re-crystallization
- reduce “orange peel” effect after mechanical working.
- Controlling the grain growth

Grain refiner (Ir, Ru, Re)

Ir

- high melting point (2447 °C),
- miscibility gap in the liquid phase
- reduced solubility (less than 0.1 wt.%) in the solid phase

How a grain refiner works



AlSi7Mg0.3 alloy
(i.e. 7 wt% Si and 0.3 wt% Mg, Al balanced)

Procast	ThermoCalc
Liquidus and solidus temperature	Liquidus and solidus temperature
Solid fraction	Solid fraction
Cp	Cp

VALIDATION

Thermo-Calc Database Description Form

TTAl5

TT Al-based Alloys Database

(Version 5.0, Jan. 2006)

Producer: ThermoTech Ltd., Surrey Technology Center, Guildford ,UK

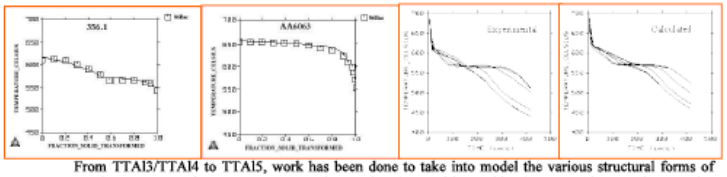
Contact person: Nigel Saunders, ThermoTech Ltd., Surrey Technology Center, Guildford, UK
Pingfang Shi, Thermo-Calc Software AB, Stockholm, Sweden

Description: This database has been developed by ThermoTech, and presents a comprehensive database for Al-alloys with a proven track record. It can be used for all major types of commercial Al-alloys ranging from commercial pure Al to complex alloys such as AA339.1, AA7075. *Note that it is originally called as Al-DATA.*

The database successfully predicts precipitation hardening reactions and provides excellent results for solution phase treatment temperatures and the formation of the "insoluble" compounds formed as part of the solidification process.

One of the striking successes of the database concerns prediction of the non-equilibrium solidification behavior of Al-alloys. Excellent agreements between the calculated results (f_s *vs* T) and experimental data from for instance Backerud *et al.* (1986) can be obtained using the SCHEIL module in the TCC and TCW software. The simulation also allows properties like heat evolution and the segregation patterns to be successfully predicted.

The phases predicted to form during the solidification process are well matched (as illustrated below). It is clear that the database provides very accurate predictions for the solidification behavior of Al-alloys in conditions that are well away from those associated with equilibrium. This provides a stringent test of the capabilities of the TTAl database that it passes remarkably well.



From TTAl3/TTAl4 to TTAl5, work has been done to take into model the various structural forms of Al3M compounds, DO22, DO23 and L12 that form with combinations Sc, Ti, V and Zr. Also beginning work on the addition of Rare Earth elements to Al-DATA.

Systems: The database (Version 5.0) contains the following 17 elements (from TTAl4 to TTAl5, La-Sc are added):

Al B C Cr Cu Fe La Mg Mn Ni
Sc Si Sr Ti V Zn Zr

The phases that are included in the database are list below:

Liquid, Al(fcc), Si, Graphite, SiC, $(Al,Ti)B_2$, Al_4C_3, Al_7Cr, Al_2Cu, Al_2CuMg, $Al_3(Fe,Mn,Ni,\ldots)$, Al_3Mg_2, $Al_6(Mn,Fe,Cu,\ldots)$, Al_3Ni, $Al_3(Ni,Cu)_2$, Al_4Sr, Al_2Si_2Sr, $Al_3(Ti,V,Zr,\ldots)$, Mg_2Si, Mg_2Zn, MC_carbide, $Al_{18}(Cr,Mn)_2Mg_3$, $Al_{13}Cr_4Si_4$, Al_7Cu_2Fe, $Al_{20}Cu_2Mn_3$, Al_7Cu_4Ni, $Al_9(Fe,Ni)_2$, α-AlFeSi, β-AlFeSi, α-$Al(Fe,Mn,Cu,Cr,\ldots)_2Si$, $Al_2Mg_3Zn_3$, Al_4SiC_4, Al_8SiC_7, $Al_5Cu_2Mg_8Si_6$, $Al_8FeMg_3Si_6$, Laves, Al_2CuMg, $Al_5(Fe,Mn,\ldots)$, $Mg(AlCuZn)_2$, E_AlCrMgMn, T_AlCuMgZn, TiC. From TTAl4 to TTAl5, added new REE phases are: $Al_{11}RE_3$, AL_3RE_DO19.

The Al-Cu-Mg-Zn quaternary has been reassessed based on its early version, so that is it fully compatible with the TTMg database.

Applications: Al-based alloy design and engineering.

Availability: Commercially available for uses with TCC and TCW.

References: Backerud L., Krol E., and Tamminen J. (1986) Solidification Characteristics of Aluminium Alloys, Vols 1 and 2, Tangen Trykk A/S, Oslo.
Saunders N. and Miodownik A.P. (1998) *CALPHAD (Calculation of Phase Diagrams): A Comprehensive Guide.* Cambridge.

TTAL8 ThermoTech

Al-based Alloys

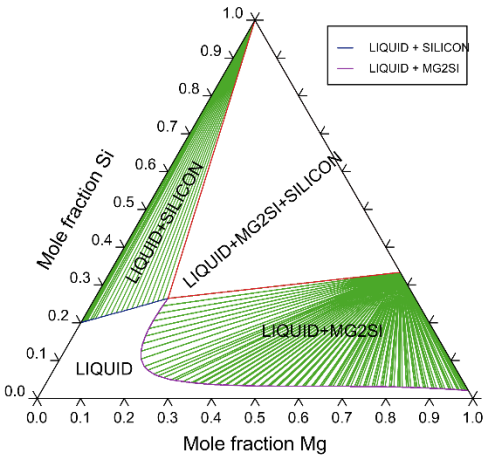
Database version 5.1 has been used for calculation.

17 ELEMENTS

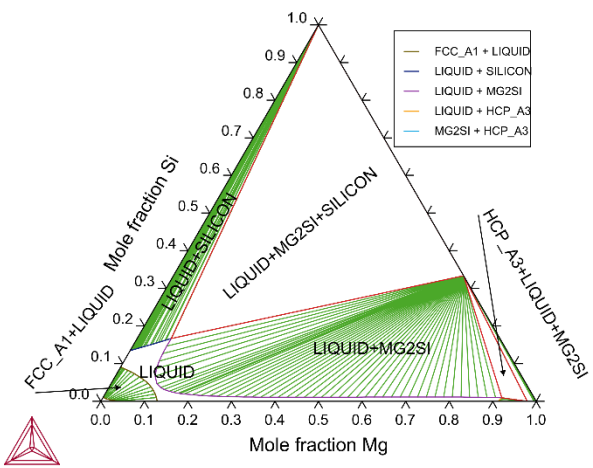
PHASES

Isothermal section of a ternary Al-Si-Mg system

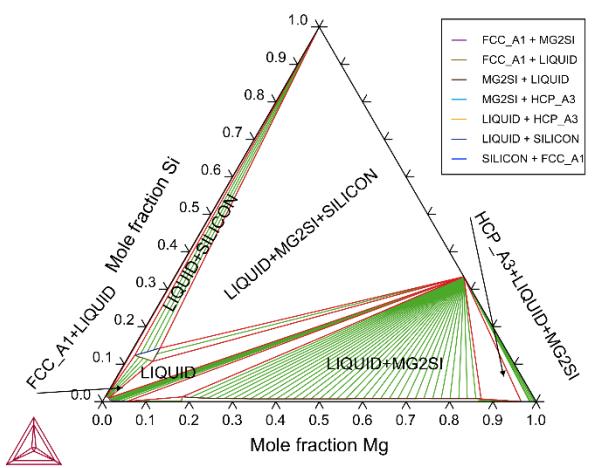
700°C



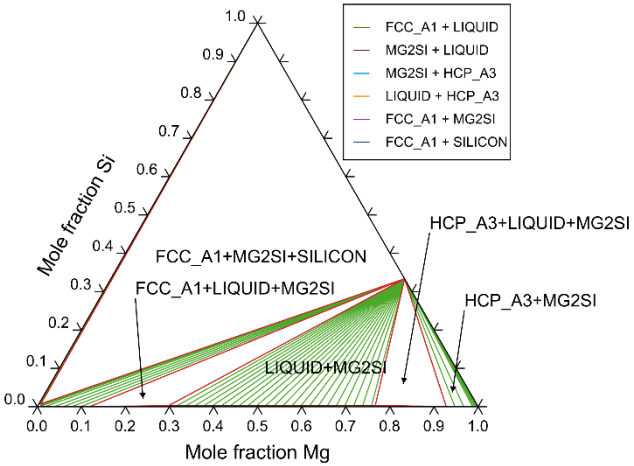
600°C



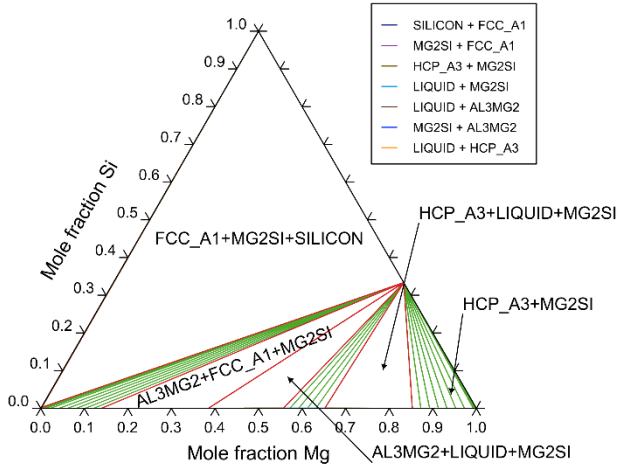
572°C



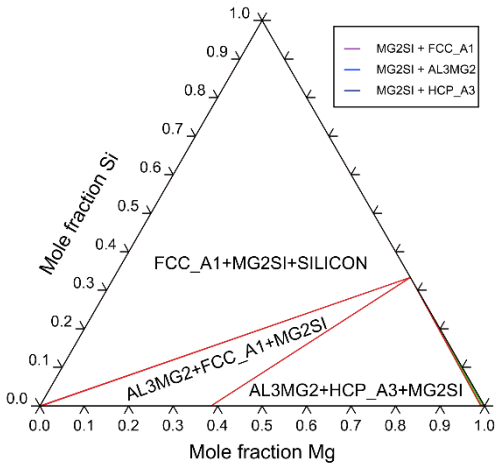
500°C



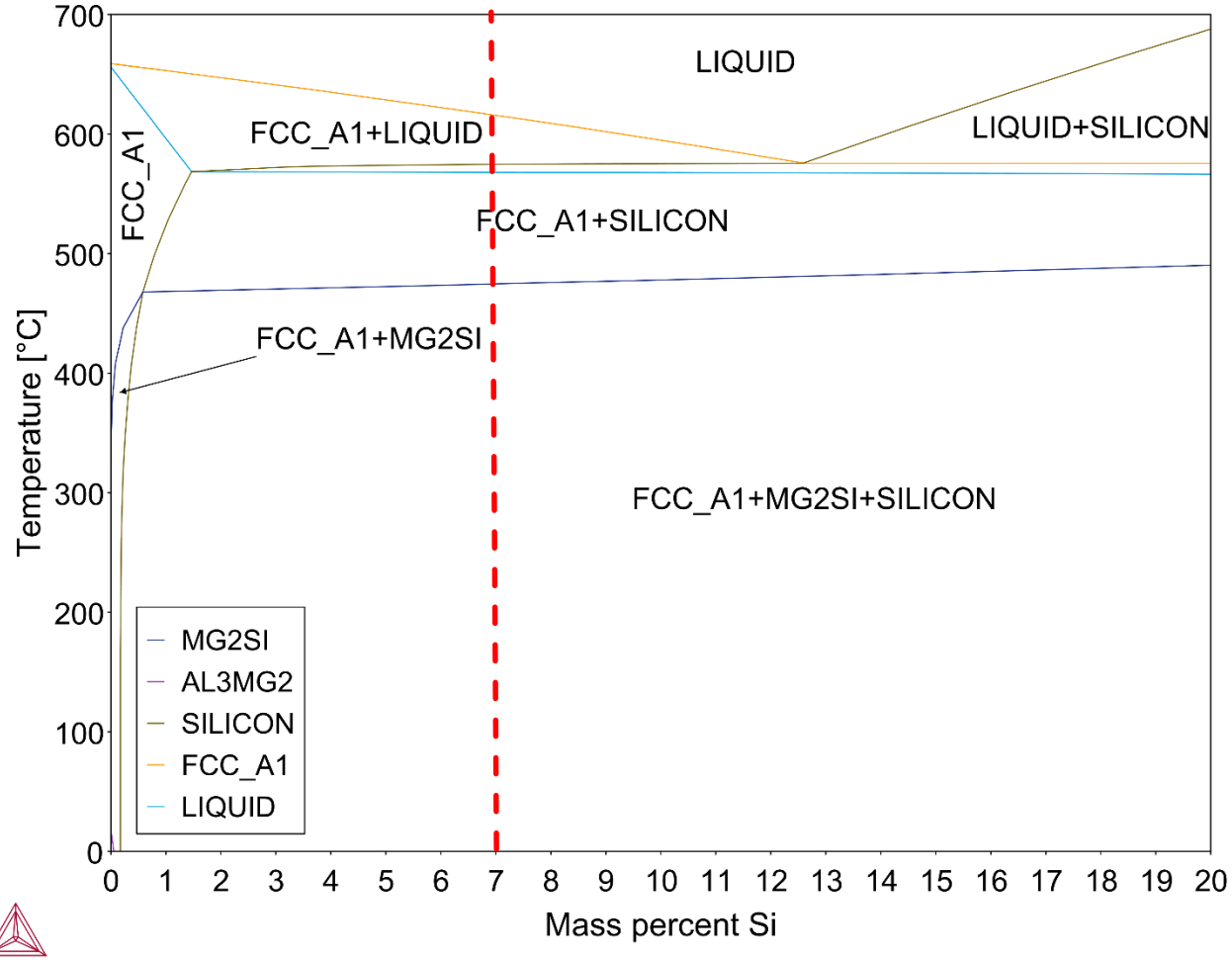
400°C



20°C



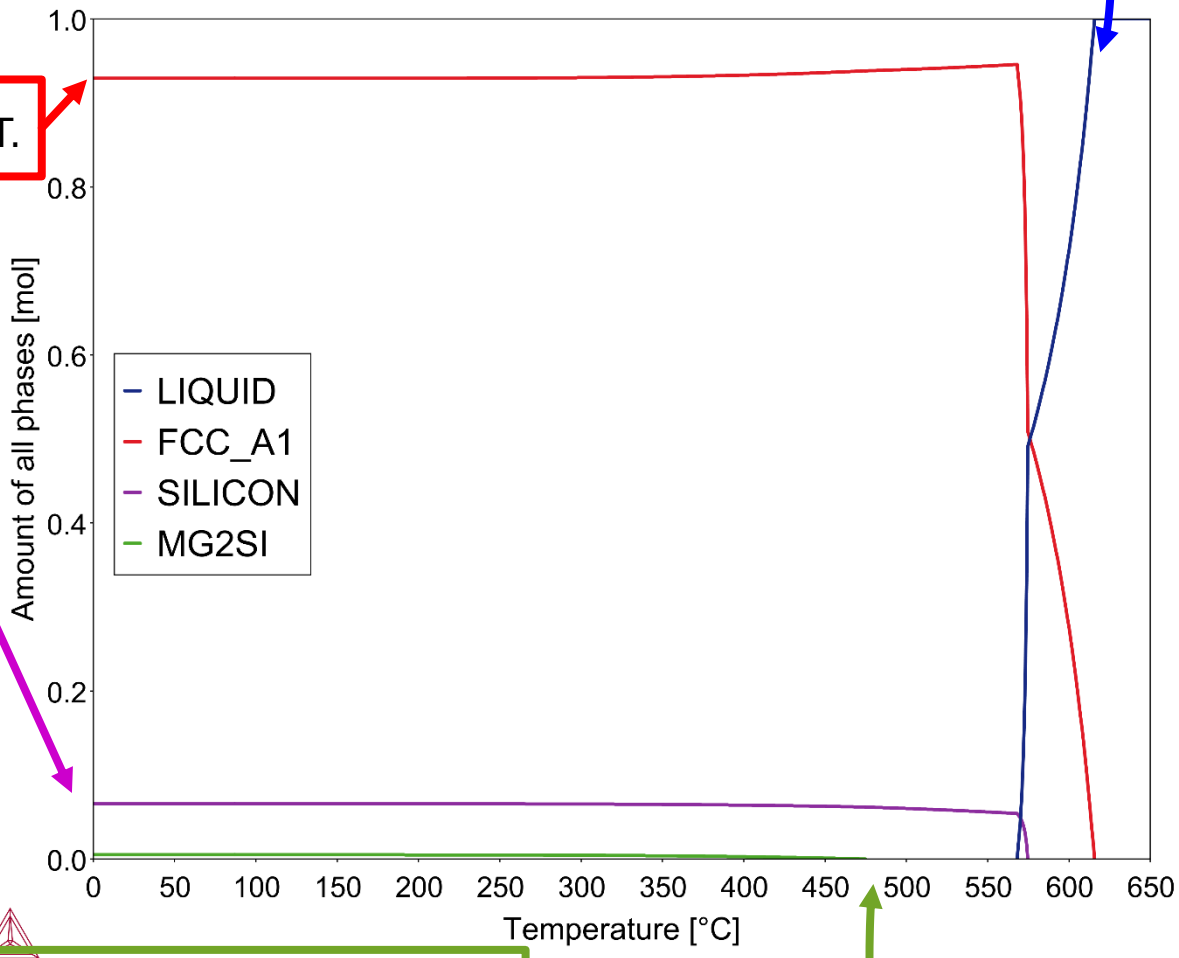
Pseudo-binary phase diagram of AlSi7Mg0.3 alloy



- All stable phases in the system considered;
- No suspended phases options applied.

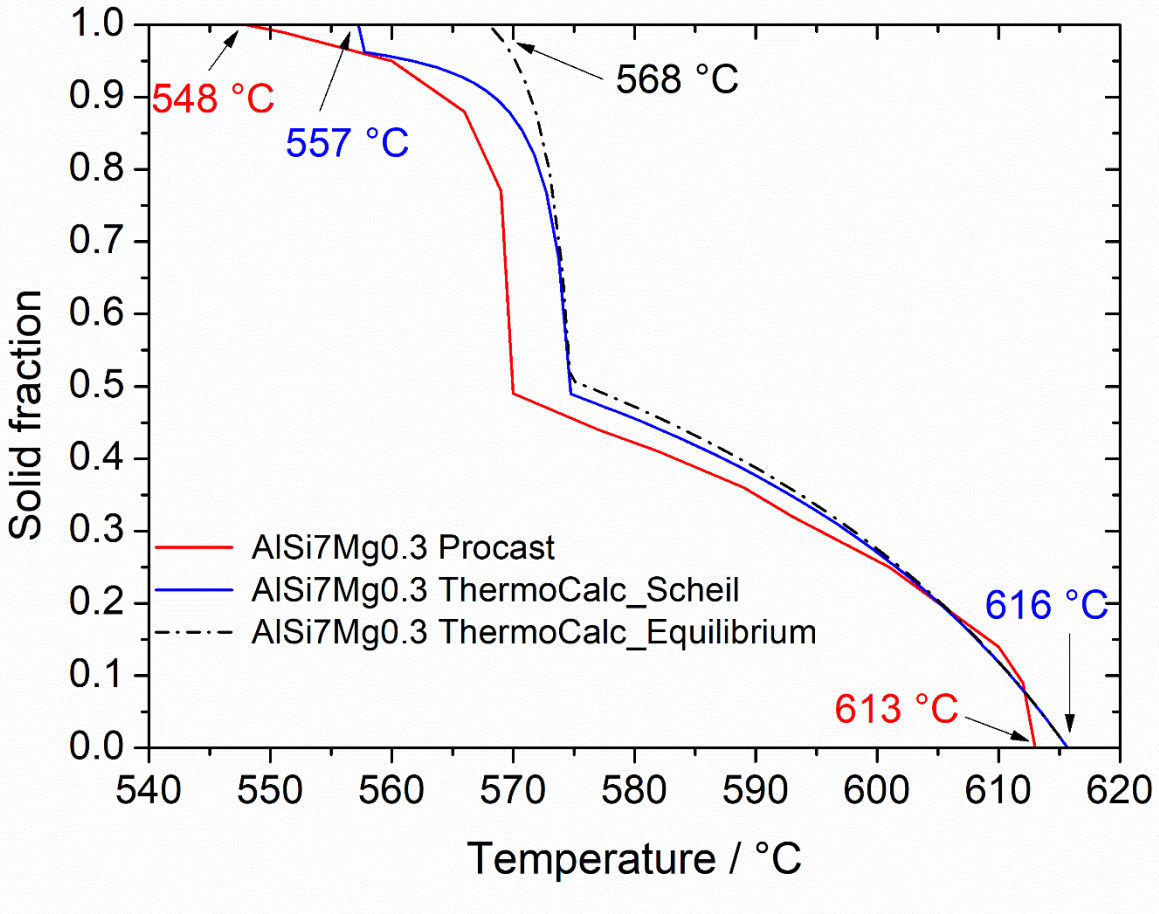
Phase fraction vs temperature

- At 616 °C, an fcc solid solution (red line) crystallises and its amount increases at the expense of the liquid phase (blue line).
- An fcc fraction of 92 % at RT.
- The remaining part of the liquid phase solidifies as silicon at 576 °C (purple line).
- At 475 °C, Mg_2Si (green line) precipitates with a small fraction (maximum 0.5 %) at room temperature.



Liquidus, solidus and solid fraction

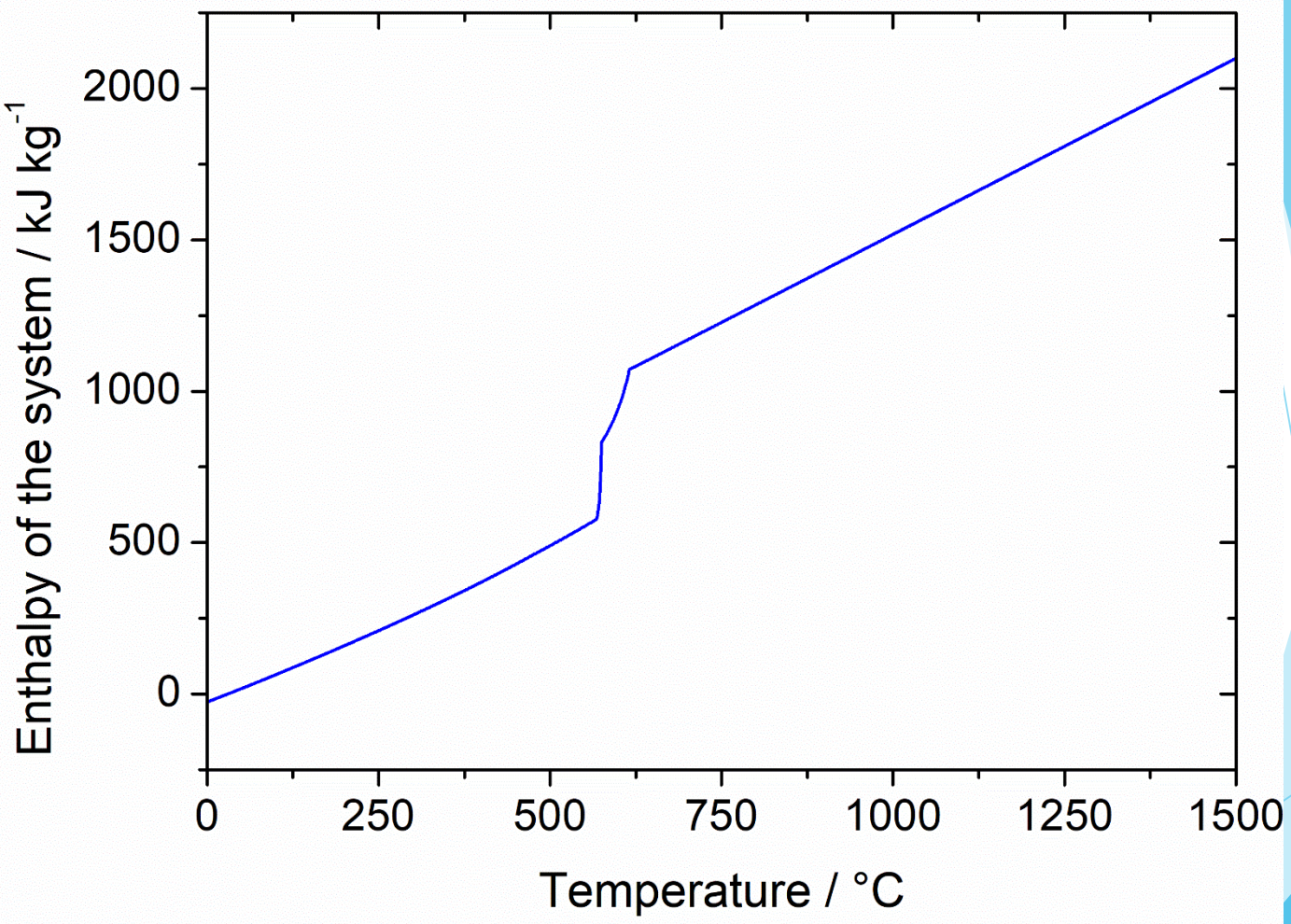
	Liquidus temperature / °C	Solidus temperature / °C
Procast	613	548
ThermoCalc (Scheil)	616	557
ThermoCalc (Equilibrium)	616	568



Scheil Model:

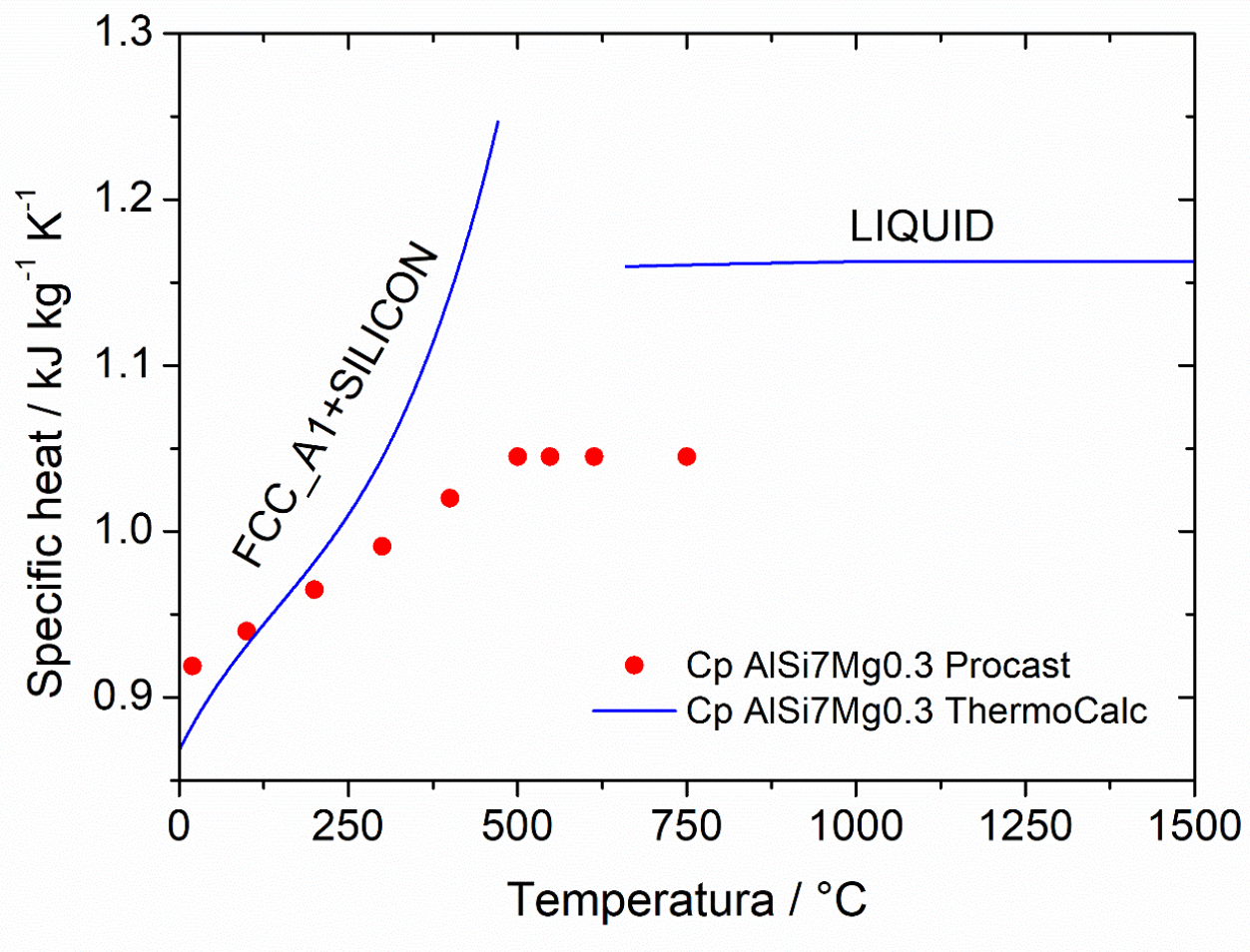
- No diffusion in solid phase;
- infinite diffusion in liquid phase at all T;
- equilibrium reached at solid-liquid interface.

Enthalpy of the system



- ThermoCalc software calculates the thermodynamic functions considering H=0 at 300 K as a reference.

Specific heat of the system (Procast vs ThermoCalc)



- In the whole range of temperature, Cp calculated with ThermoCalc is higher than that obtained with Procast.
- Stable phases are labelled in the plot;
- Discontinuity due to phase transitions.

18 K Au-based alloy 2504

Composition

Au	Ag	Ir	Zn	Cu
In millesimal				
750	45	0.09	0.5	bal.
In wt. %				
75	4.5	0.009	0.05	bal.

21 Elements

204 binary systems
61 ternary systems

321 solutions and intermetallic phases

TCNOBL1 Database

TCNOBL1: TCS Noble Metal-based Alloy Database

Database name:	TCS Noble Metal-based Alloy Thermodynamic Database	*Database acronym:*	TCNOBL
Database owner:	Thermo-Calc Software AB	*Database version:*	1

TCNOBL1 is a thermodynamic database developed by Thermo-Calc software for noble (or precious) metal-based alloys. It is intended for applications in jewelry, dental alloys, decoration industries, and delicate components in scientific instruments.

Included Elements (21)

Ag	Al	Au	Co	Cr	Cu	Fe	Ga	Ge	In	Ir
Mn	Ni	Pd	Pt	Re	Rh	Ru	Sn	Ti	Zn	

A hybrid approach of experiments, first-principles calculations and CALPHAD modeling are used to obtain thermodynamic descriptions of the constituent binary and ternary systems over the whole composition and temperature ranges.

In total, 204 binary systems and 61 ternary systems are assessed. These assessed binary and ternary systems can be calculated with the BINARY module and the TERNARY module in Thermo-Calc, respectively.

- TCNOBL1 Assessed Binary Systems
- TCNOBL1 Assessed Ternary Systems

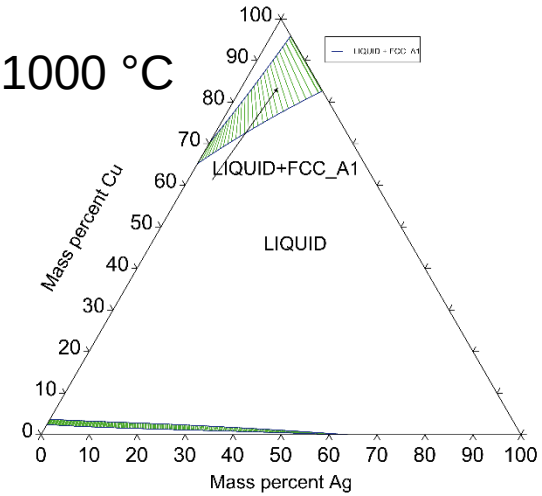
TCNOBL1 contains 321 solution and intermetallic phases in total, which includes nearly all stable phases in the assessed systems that may form in as-cast and aged noble-based alloys. A full list of the phases and their models and constituents can be found in Included Phases in TCNOBL1.

The database can be used to calculate various phase diagrams and property diagrams in the assessed systems or even extrapolated higher-order systems. The extrapolation to higher-order systems helps to understand the phase equilibria in multi-component industrial noble alloys, so as to predict the phase formation, phase fractions and phase compositions or to calculate the driving force of forming a phase. The database can also be used for predicting solidification behavior of noble alloys with the SCHEIL_GULLIVER module in Thermo-Calc and simulating general diffusion controlled phase transformations with the Diffusion Module (DICTRA) or multi-particle precipitations during aging treatment with the Precipitation Module (TC-PRISMA).

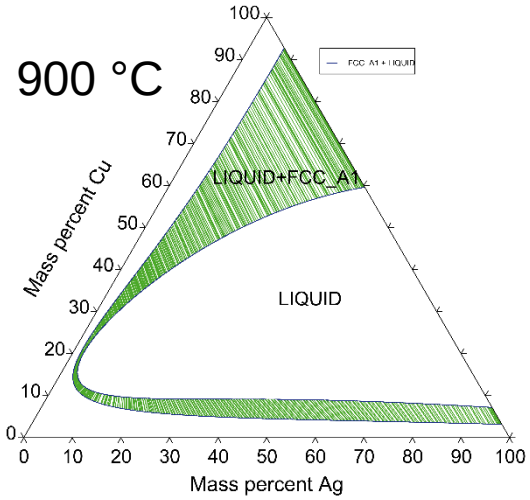
2504 ALLOY

Building the phase diagram

1000 °C

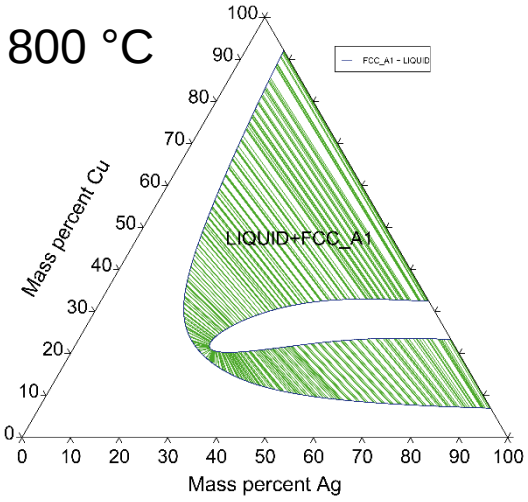


900 °C

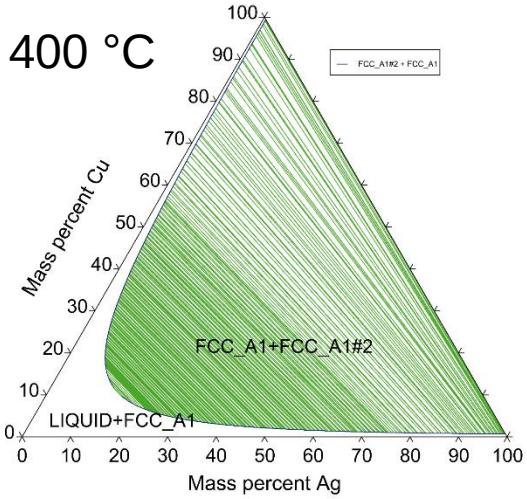


Ternary system Au-Cu-Ag

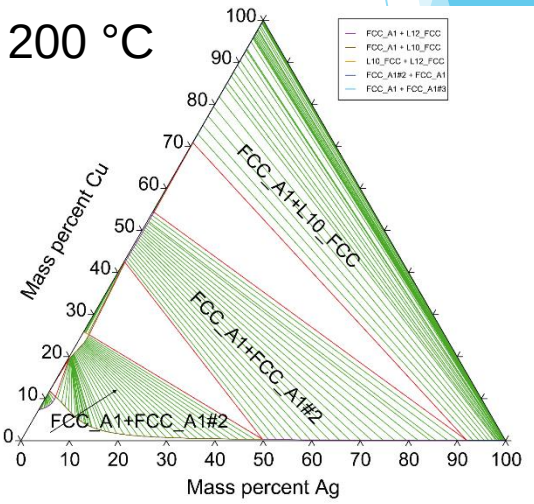
800 °C



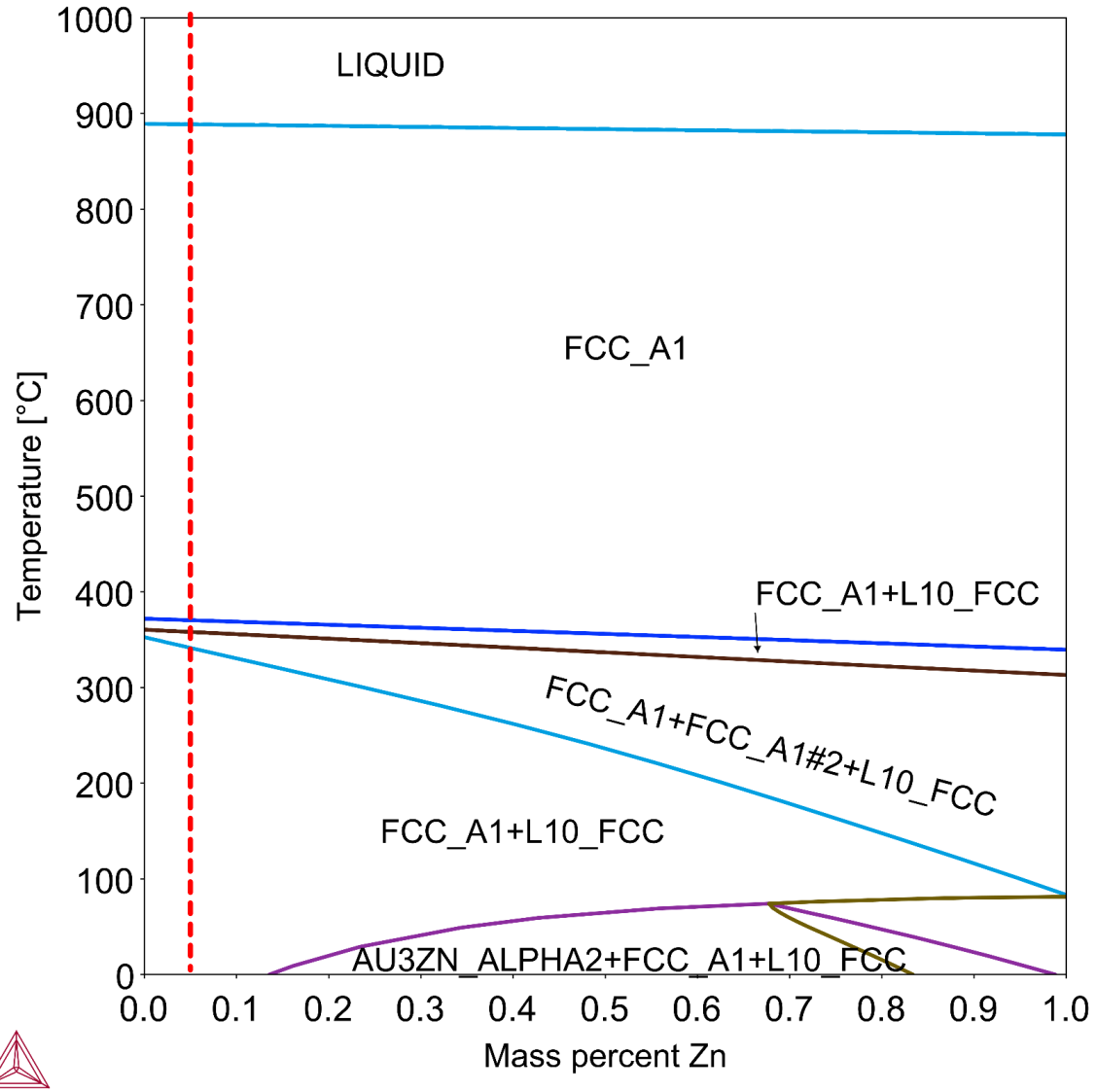
400 °C



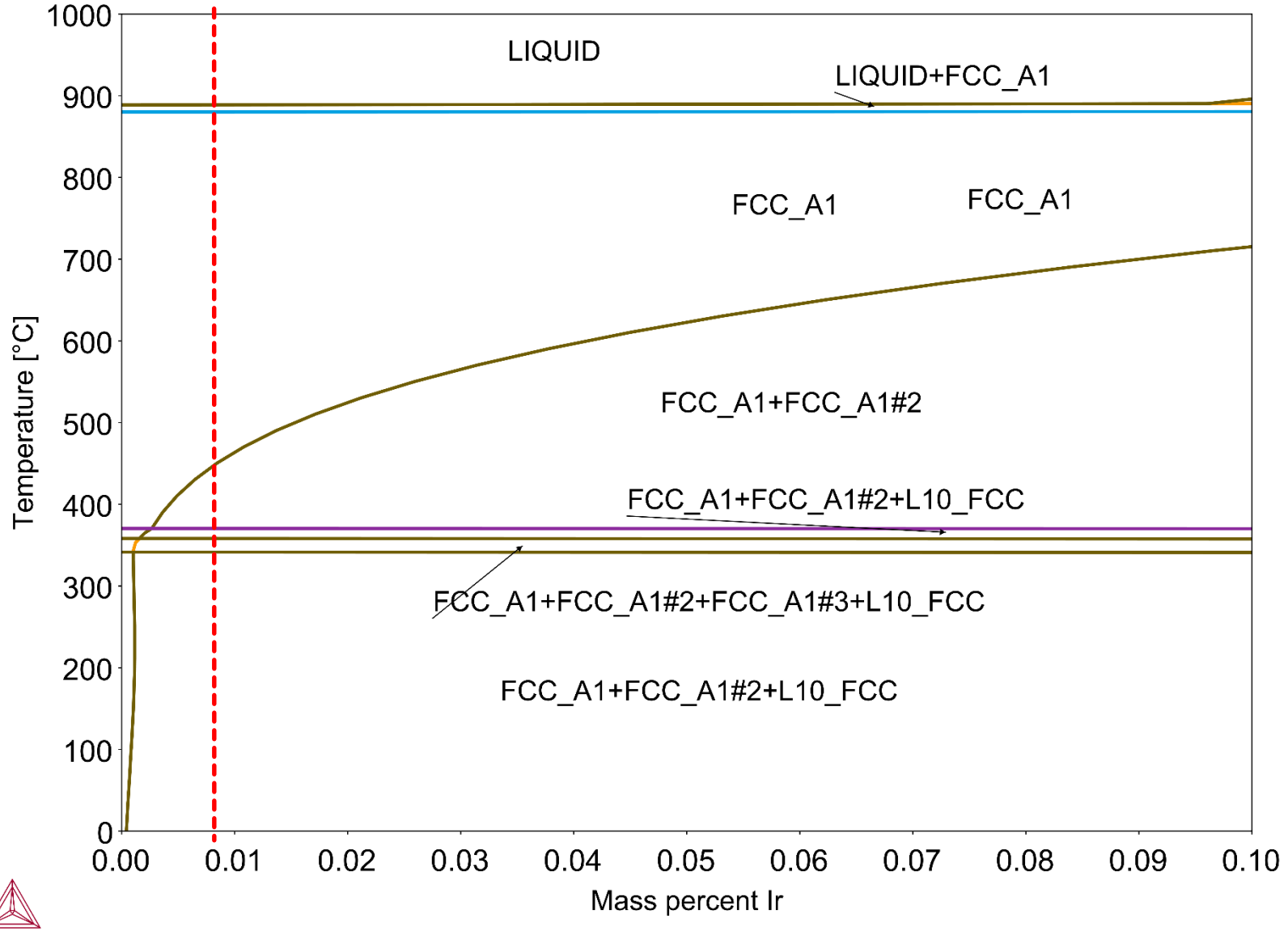
200 °C



Quaternary system Au-Cu-Ag-Zn



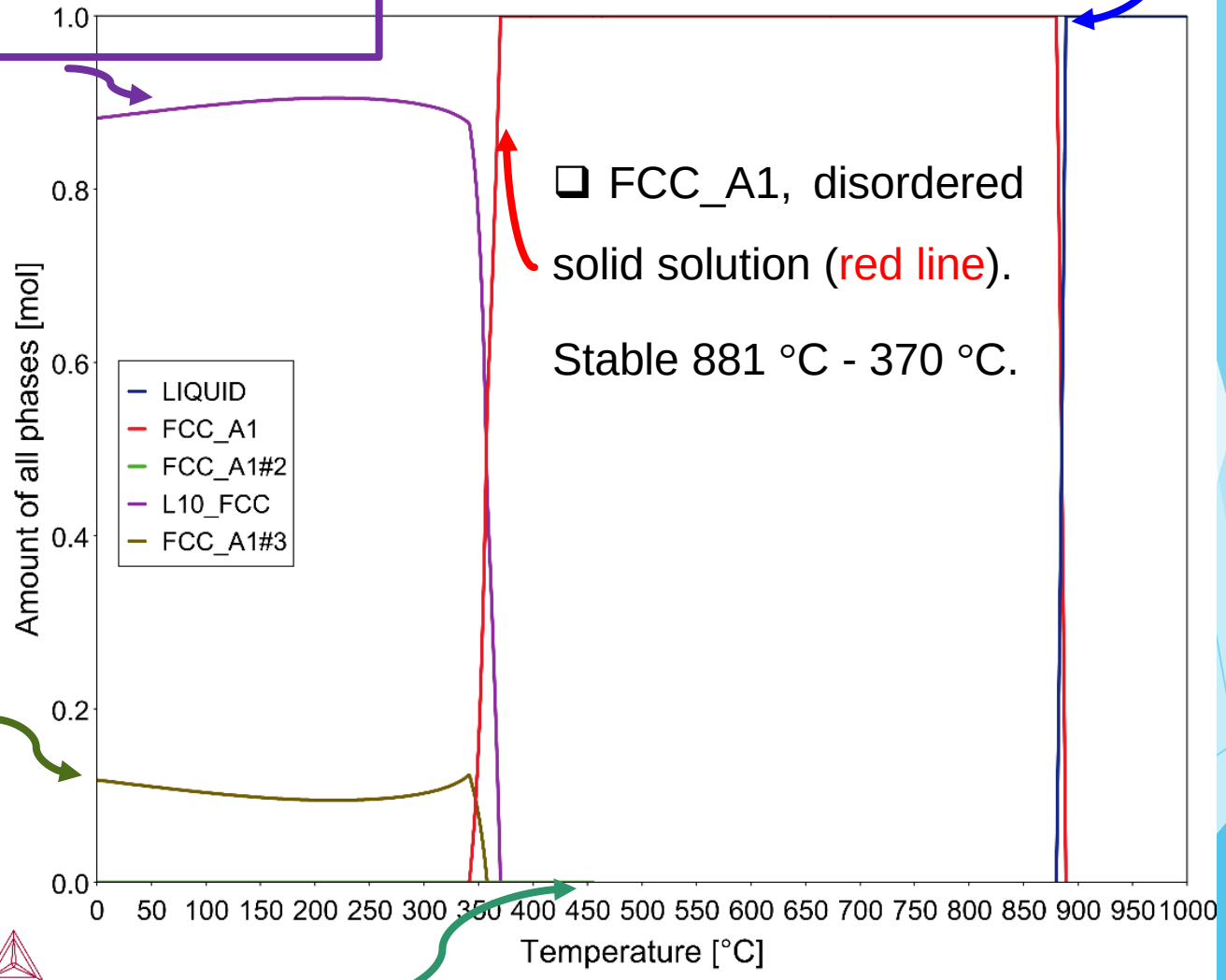
Quinary system
Au-Cu-Ag-Zn-Ir



Phase fraction vs temperature

❑ Liquid (blue line) and liquidus at 889 °C

❑ Ordered solid solution L10_FCC (violet line).



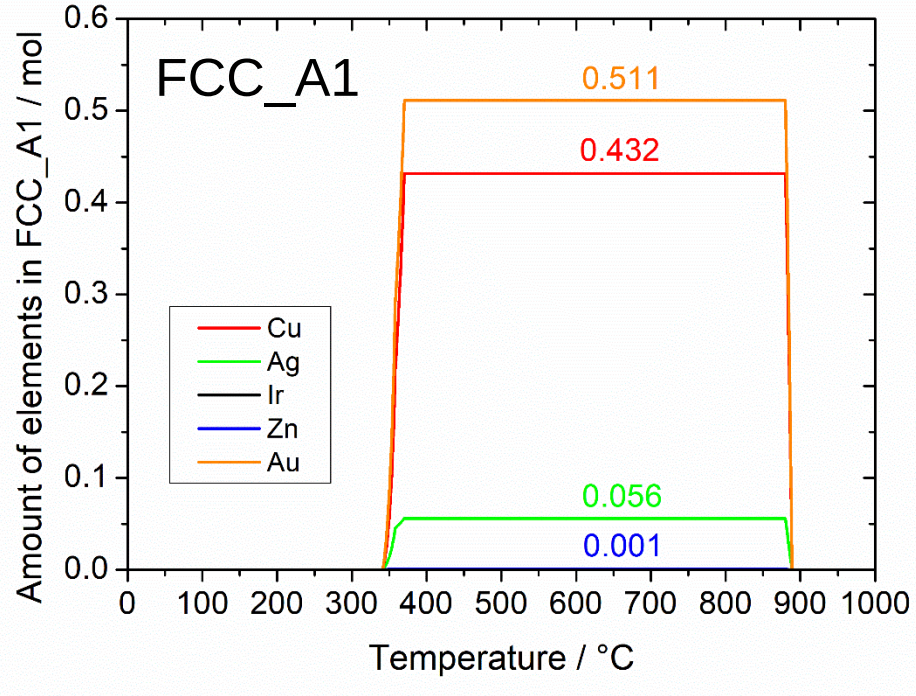
❑ FCC_A1, disordered solid solution (red line).

Stable 881 °C - 370 °C.

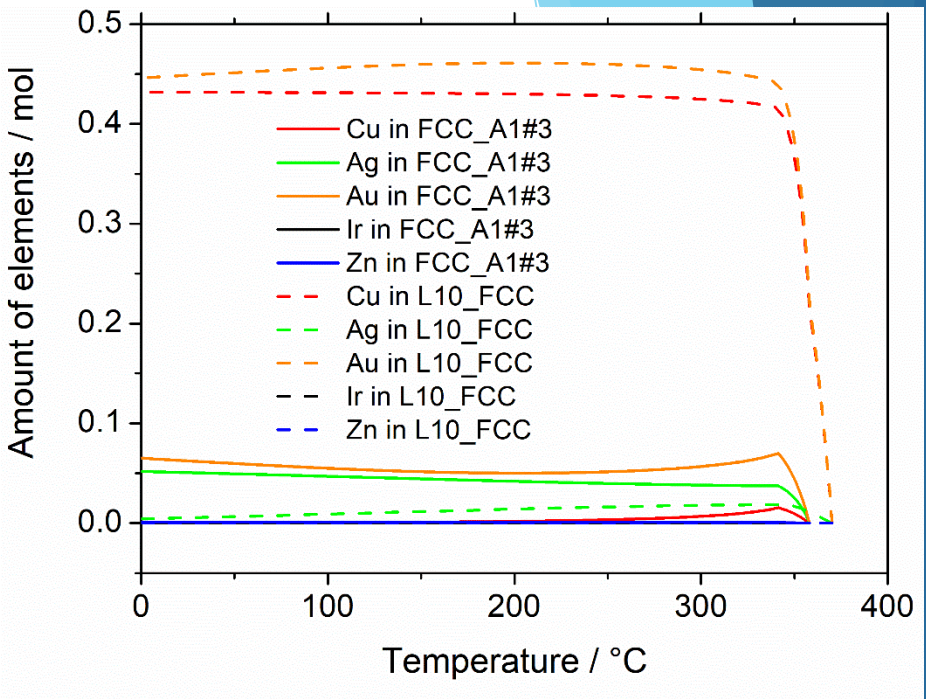
❑ Disordered solid solution an FCC_A1#3 (olive green line).

❑ Disordered solid solution FCC_A1#2, if its amount is rather limited.

Phases composition



FCC_A1#3 and L10_FCC



- it derived from fcc structure;
- corners and the corresponding face in the same plane are occupied by one type of atoms;
- the other faces between two planes are occupied by a second type of atoms.

$L1_0$ prototype structure: CuAu

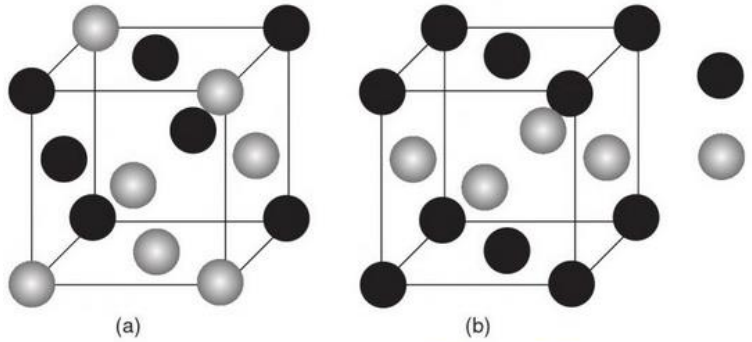
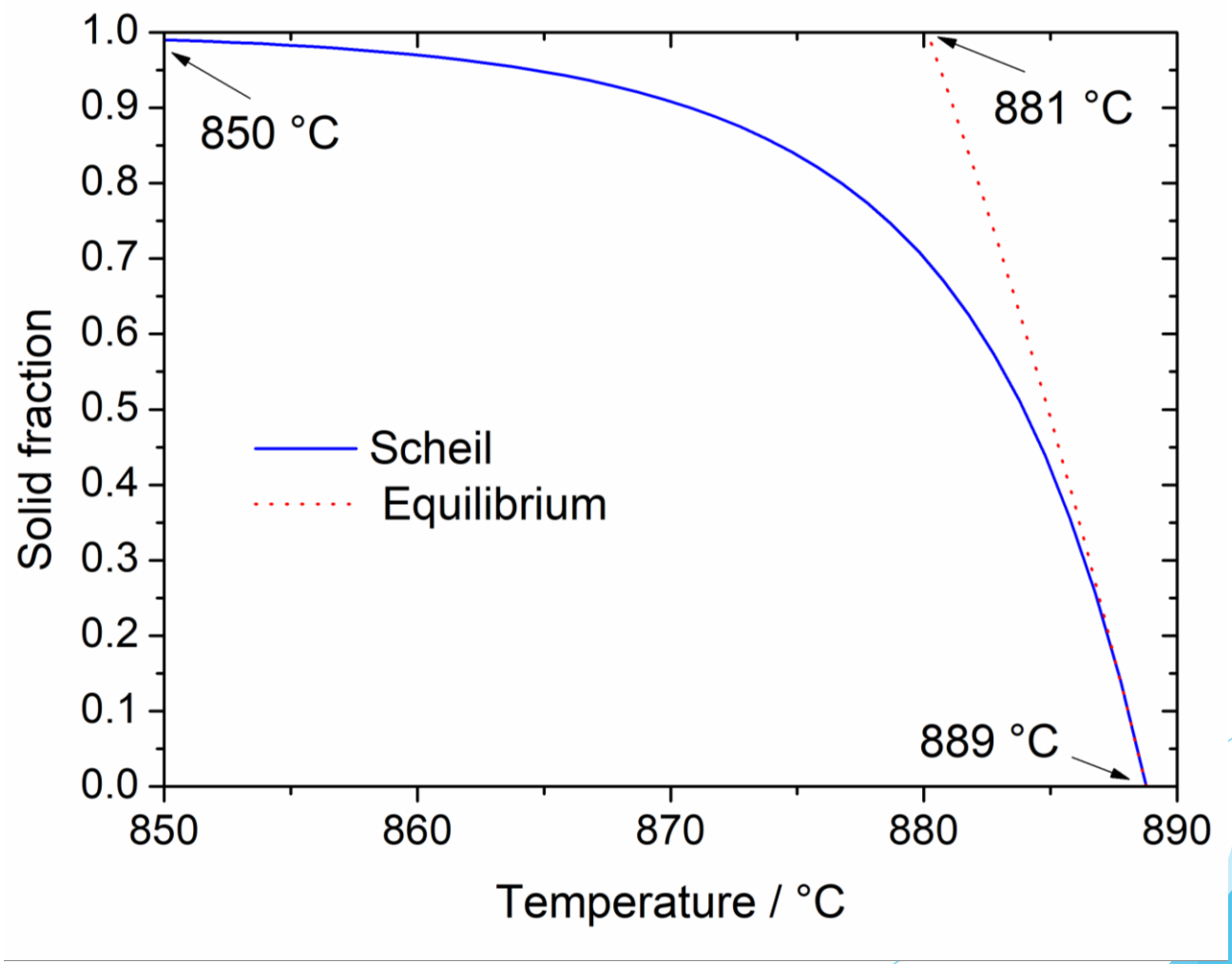


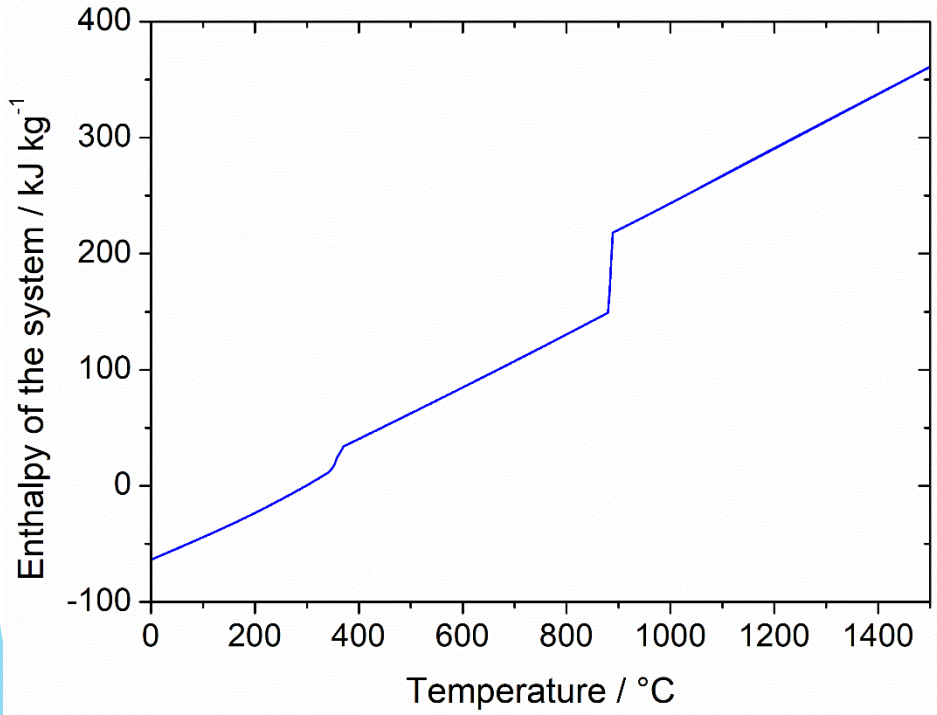
Figure 11.1. Schematics of (a) fcc and (b) $L1_0$ structures.

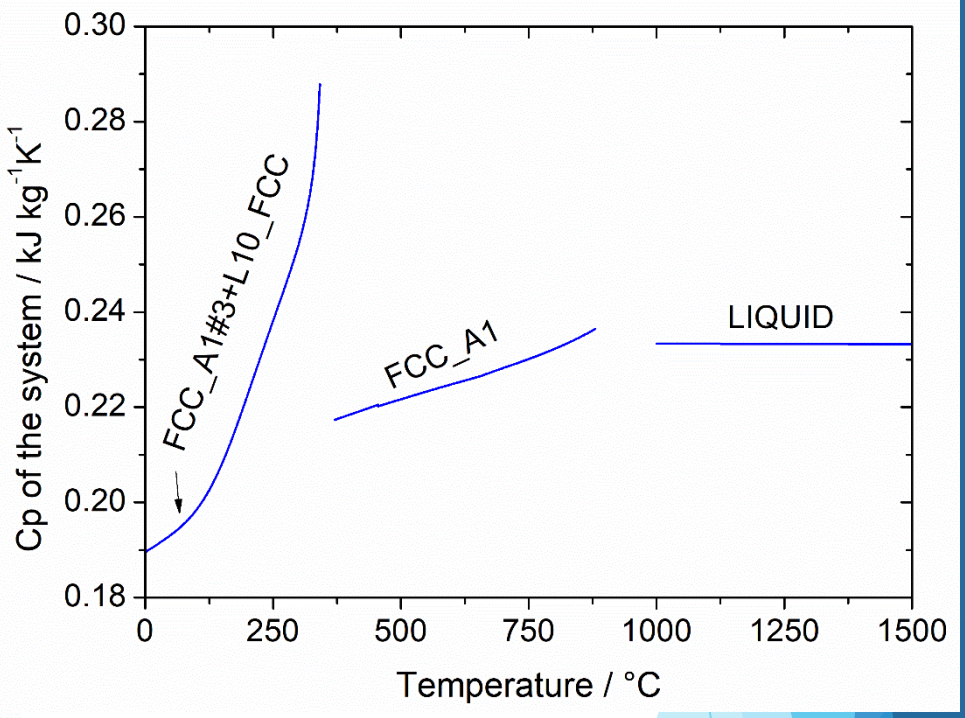
Liquidus, solidus and solid fraction

ThermoCalc	Liquidus temperature / °C	Solidus temperature / °C
At the equilibrium	889	881
Scheil model	889	850



Enthalpy and specific heat of the system





- ThermoCalc software calculates the thermodynamic functions considering H=0 at 300 K as a reference.

CONCLUSIONS

- ThermoCalc software was applied to calculate thermodynamic parameters of two alloys.
- A standard alloy of composition AlSi7Mg0.3 was investigated and results have been compared with outputs obtained by the Procast software for the same alloy.

- This validation step was an useful exercise to match the two softwares:
  - ✓ good agreement found among ThermoCalc results and Procast outputs;
  - ✓ starting point to support results related to an alloy of interest, never assessed with Procast, but whose thermodynamic parameters are object of interest.

CONCLUSIONS

- The alloy of interest is an 18 carats alloy, named 2504, containing a limited amount of Ir for grain refining.
Thermodynamic parameters calculated by ThermCalc:
  - ✓ Pseudo-binary phase diagram
  - ✓ Phase fraction vs temperature
  - ✓ liquidus and solidus temperature
  - ✓ Solid fraction (Scheil model)
  - ✓ Enthalpy and specific heat of the system

- These parameters are a first step forward to study the thermodynamic conditions for the formation of Ir precipitates in 18 K gold alloys for a better control of the grain size.

Thanks for your attention!