

# The Intermetallic System Cu-Ni-Sn

*H. Flandorfer, C. Schmetterer and H. Ipser*

University of Vienna

Department of Inorganic Chemistry / Materials Chemistry

## Outline

- **Why working on Cu-Ni-Sn**
- **Literature information**
  - Key papers
  - Special sections
  - Ternary compounds?
- **Our preliminary results**
  - 700 °C isothermal section
  - 400 °C isothermal section
  - 500 °C isothermal section
  - 220 °C isothermal section

## Why working on Cu-Ni-Sn


### Technical applications

- Cu-Ni alloys (Ni-bronzes) with additions of Sn as deformable alloys and conducting materials in electric devices, automobiles and household.
- Solder alloys and Ni as contact material or as a component in lead-free solder applications.

### Basic research

- Occurrence of a very special solidification behavior in the (Cu,Ni)-rich corner of the diagram

## Ag-Cu-Ni-Sn is currently the most important system for lead-free soldering!

Cu and Ni show total mutual solubility and the TM's solve significant amounts of tin. Beyond that there is practically no mutual solid solubility:  **Extended ternary**

**solubility of the binary IMC's exists only in Cu-Ni-Sn!**

From a huge amount of diffusion couple studies it turned out that the formation of ternary solid solutions of the types



have tremendous influence on the operation and performance of solder joints.

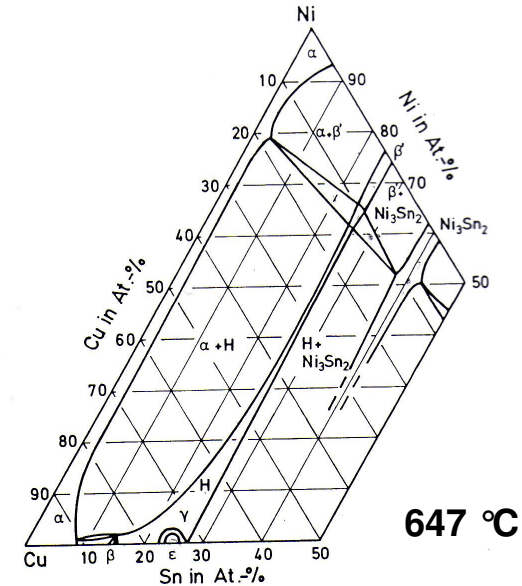
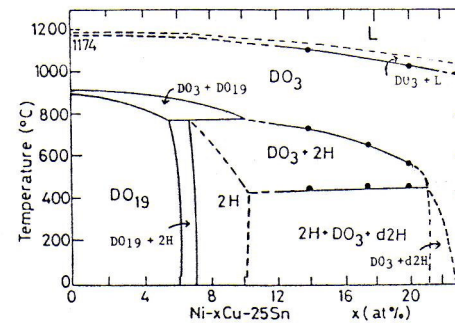
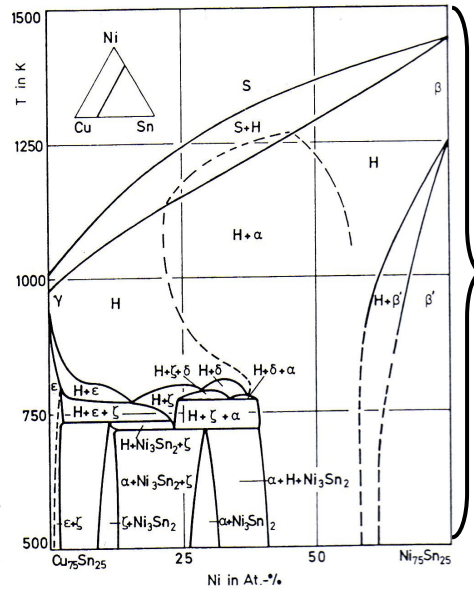
## Literature information

Earlier work was mainly concerned with the (Cu,Ni)-rich part whereas more recent publications are focused on the Sn-rich part.

### Key papers

- ***E. Wachtel and E. Bayer, Z. Metallkde., 75, (1984)***  
Isotherm at 647 °C, Isopleth at 25 at.% Sn, part. liquidus projection
- ***J.S. Lee Pak and K. Mukherjee, O.T. Tinal and H.-R. Pak, Mat. Sci. Eng., A117, (1989) and A130, (1990).***  
part. isopleth at 25 at.% Sn, two ternary phases (2H and d2H)
- ***G. Ghosh, Landolt-Börnstein, New Series IV, Vol. 11C3; MSIT®***  
Comprehensive compilation and assessment of experimental and calculated data to structure, phase relations and thermodynamics  
**129 references from 1928 to 2006, 70 describe experimental work!**

## The vertical section at 25 at.% Sn



- Low ternary solubility of the  $\epsilon$ -Cu<sub>3</sub>Sn phase
- Stabilization of phases to lower T by additions of the second TM
- Complex phase equilibria below  $\sim 500$  °C at the Cu-rich side
- Martensitic phase transformations at the Ni-rich part
- Stable ternary phases 2H ( $\beta$ -Cu<sub>3</sub>Ti type) and dH<sub>2</sub> (distorted  $\beta$ -Cu<sub>3</sub>Ti type)

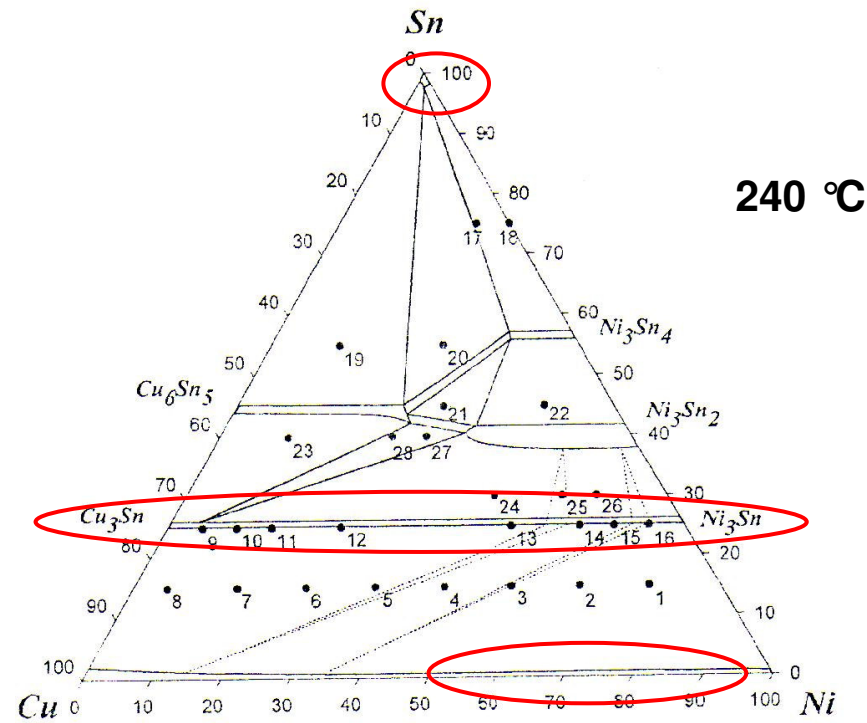
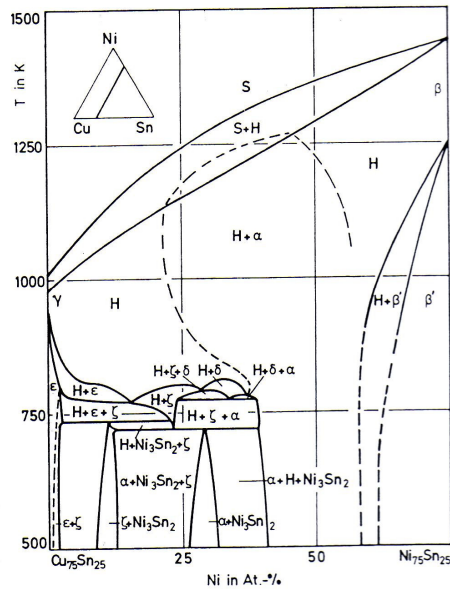
## Isothermal sections

**Many isothermal sections have been published in recent years:**

- Most of them are based on experimental data (XRD and EPMA) and calculations at low temperatures (approx. 240 °C).
- Conventional equilibration and quenching techniques are not suitable to describe phase relations below ~ 40 at.% Sn at these temperatures.
- Because of complex phase transformations, possible metastable phase transformations, coring effects, etc., the experimental investigation of the (Cu,Ni)-rich part is very difficult.
- Some of the published sections are erroneous simply from a theoretical point of view and neglect well accepted literature data published long time before.

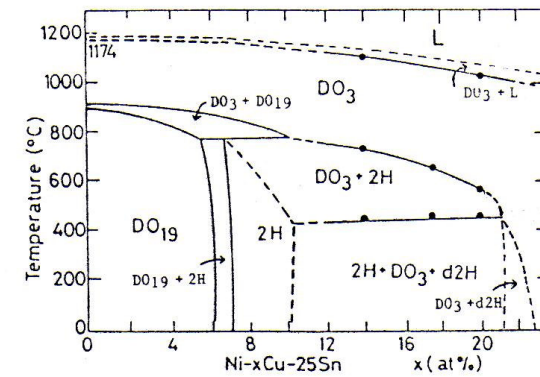
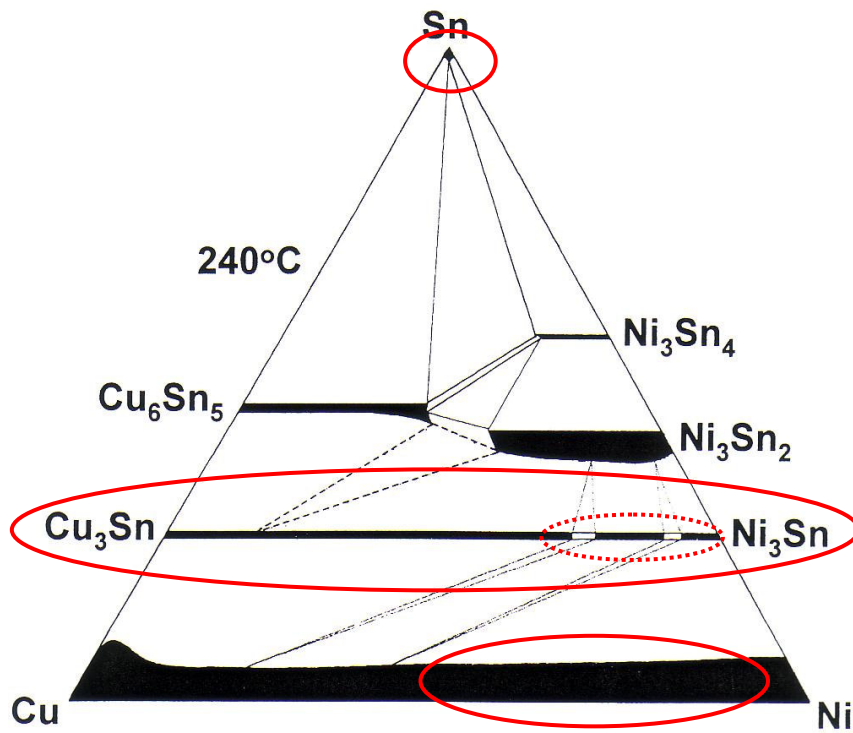


# Isothermal sections

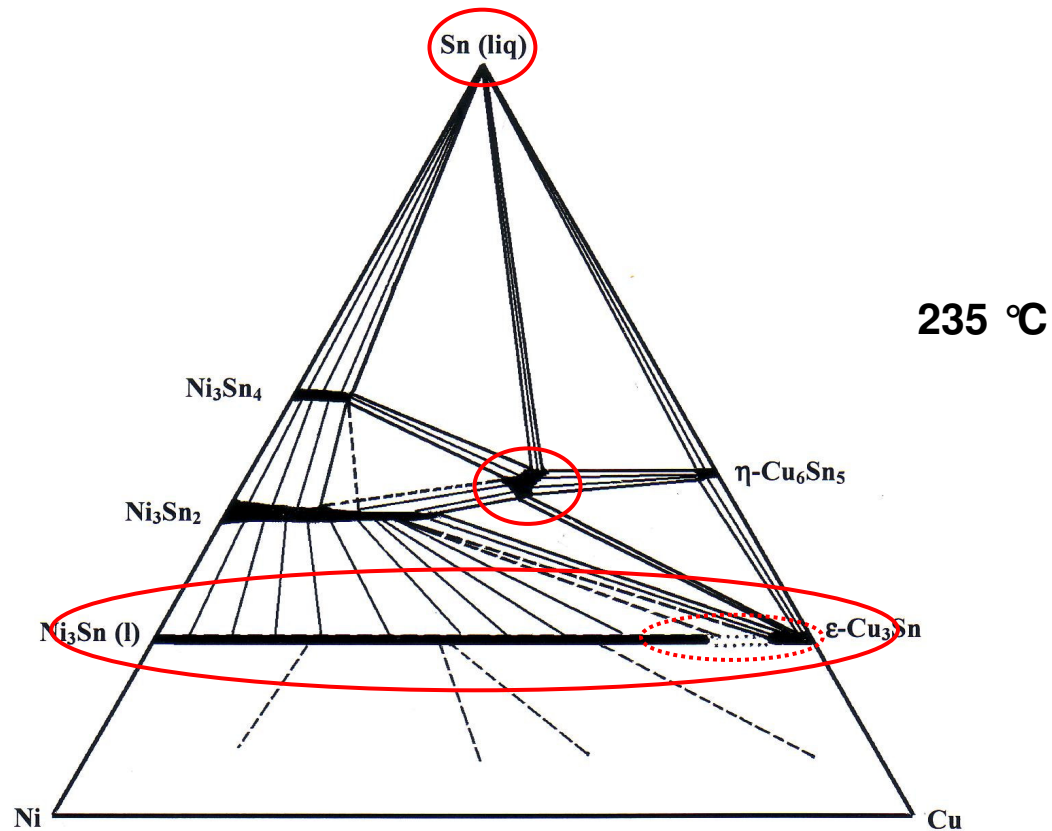




# Isothermal sections



## Isothermal sections



# Ternary compounds

Are there separate

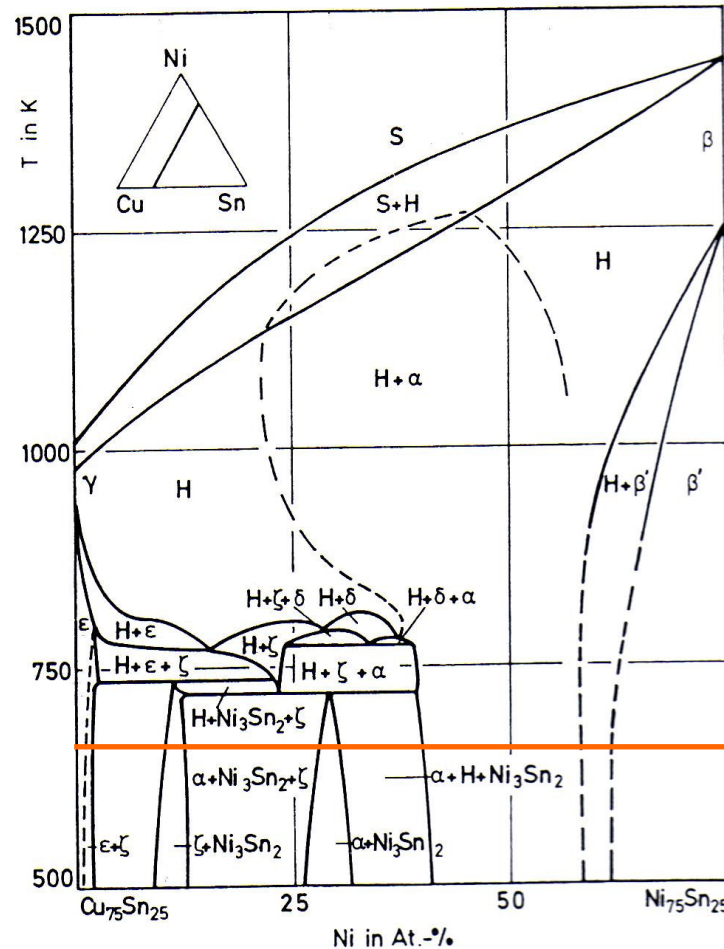
Three ternary phases

- $\text{Cu}_2\text{NiSn}$
- $\text{CuNi}_5\text{Sn}$
- $\text{CuNi}_2\text{Sn}$

Two ternary phases

- $\text{Cu}_{27}\text{Ni}_2\text{Sn}$
  - $\text{Cu}_4\text{Ni}_2\text{Sn}$
- section  
 No experimental

According to  
 existence of a



mentioned in literature:

$\text{Zr}_2\text{Ni}_3\text{Sn}$   
 from TEM and ED  
 Ti type, triclinic

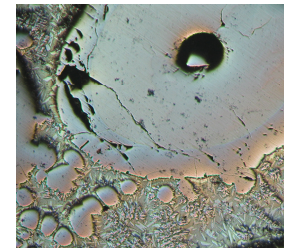
mentioned in literature:

at 235 °C (2 month)?  
 stabilities along the  
 NiAs-type phase.  
 transformation mechanism!

assessments the  
 most likely!

## Experimental challenges

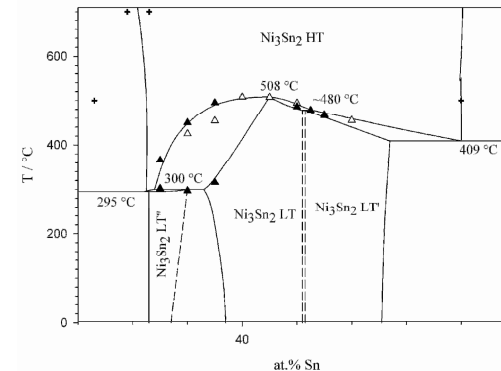
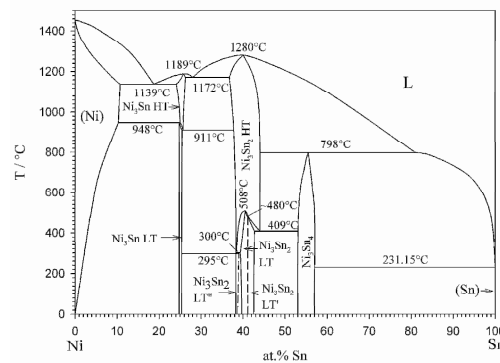
- The large difference of m.p. of Cu, Ni and in particular Sn
- The very slow dissolution of Ni in the matrix of Cu and Sn  $\Rightarrow$  difficult homogenization
- The small difference in the atomic number of Cu and Ni  $\Rightarrow$  limited distinction of different phases and structures in SEM and XRD
- Many phase transformation in a narrow concentrational region with closely related structures



## Experimental efforts

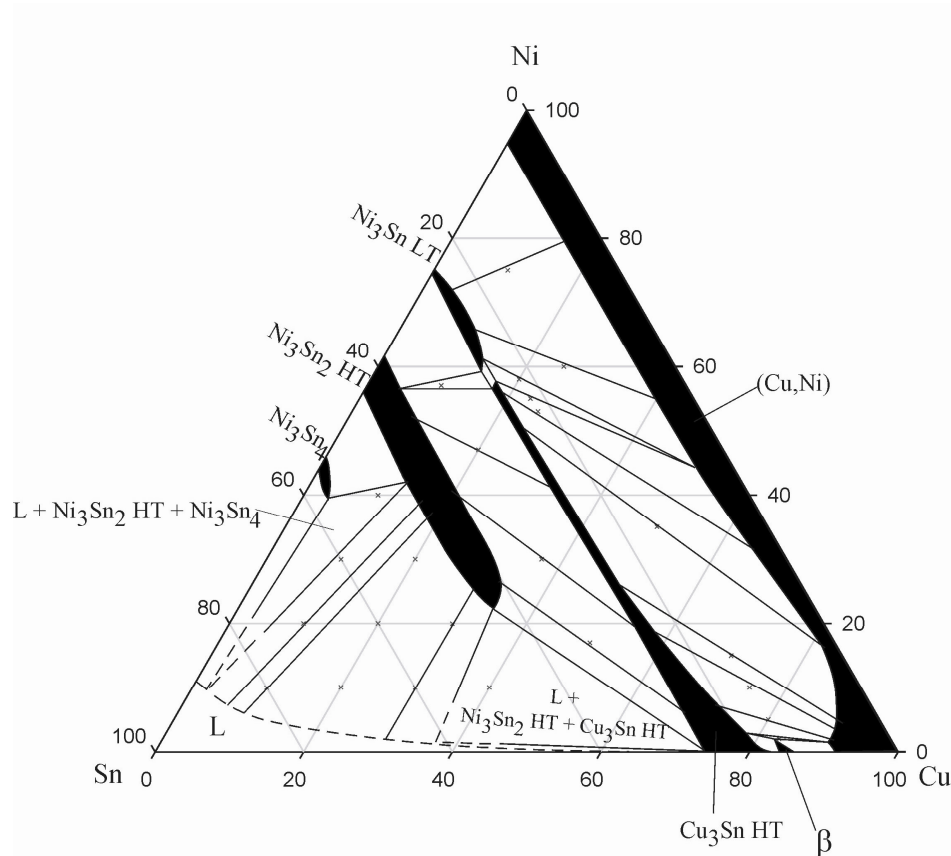
- Cross-check of Cu-Sn with 10 samples
- New investigation of Ni-Sn:

**C. Schmetterer, H. Flandorfer\*, K. W. Richter, U. Saeed, M. Kauffman, P. Roussel, H. Ipser, Intermetallics, 15, (2007), 869.**



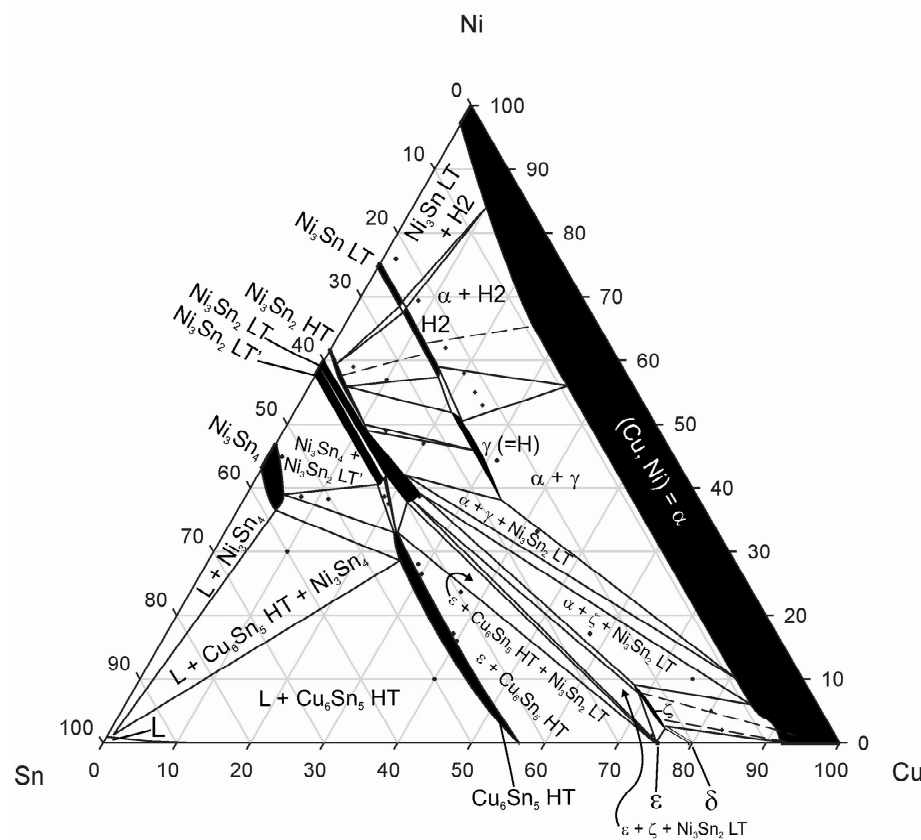
- Preparation of approx. 100 ternary samples, annealing at different temperatures  $\Rightarrow$  XRD, SEM, EPMA

## Isothermal Section at 700 °C



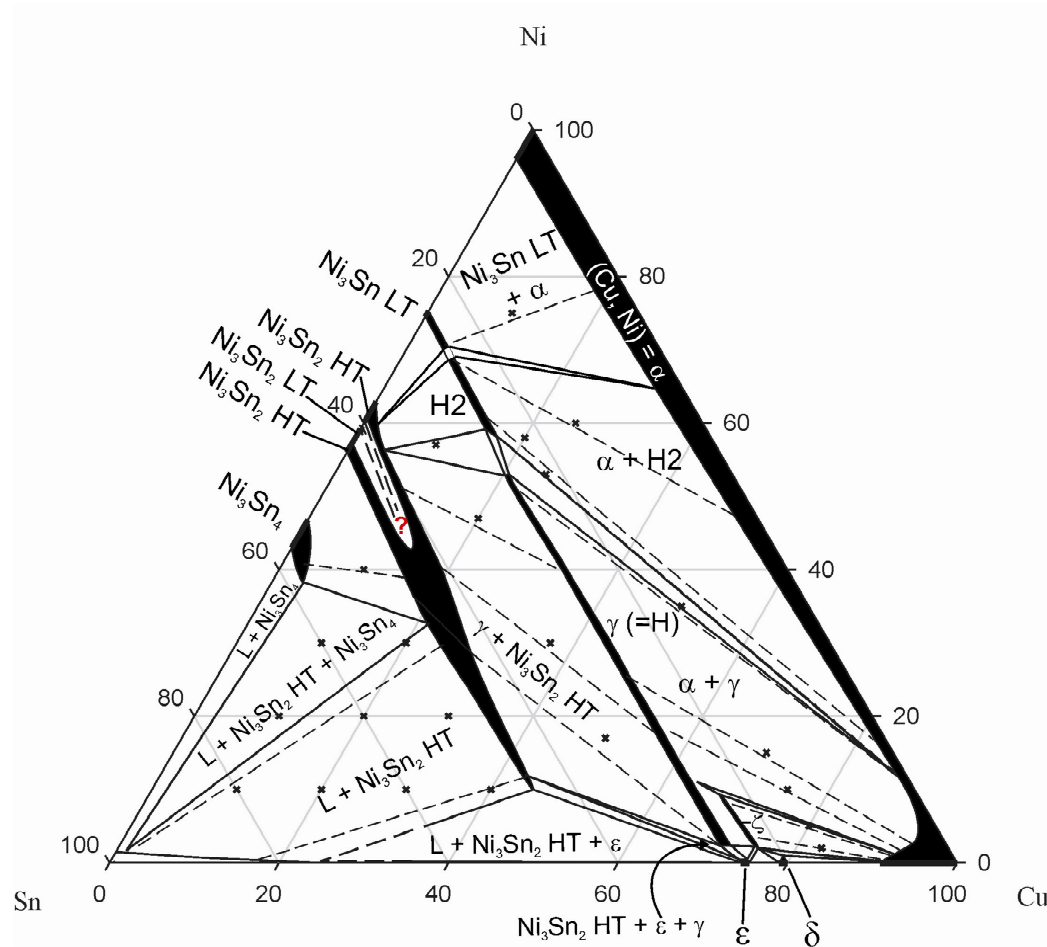


## Isothermal Section at 400 °C

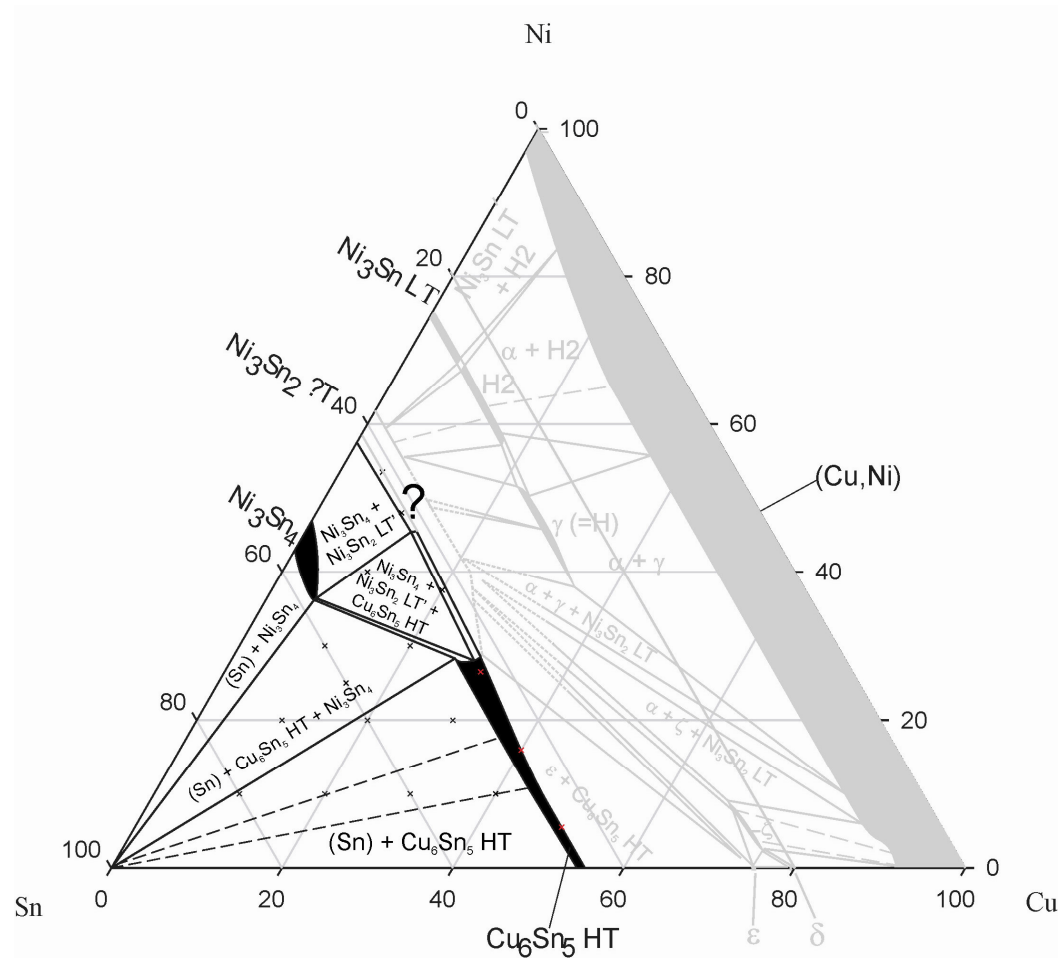




## Isothermal Section at 500 °C



## Isothermal Section at 220 °C



# Acknowledgements

## Thanks to:

- All my colleagues of the Materials Chemistry Department for the excellent collaboration
- The FWF for financing the project No. P-16495-N11
- All the co-operation partner of the project and COST-531 Action



# Thank You for Your attention!