Effect of Cooling Rate on the Intermetallic Layer in Solder Joints

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Abstract
While it has long been known that the Cu_6Sn_5 intermetallic that plays a critical role in the reliability of solder joints made with tin-containing alloys on copper substrates exists in two different crystal forms over the temperature range to which electronics circuitry is exposed during assembly and service, it has only recently been recognized that the change from one form to the other has implications for solder joint reliability. Under equilibrium conditions the change from the hexagonal to monoclinic form occurs in the cooling solder joint at 186°C. However, cooling rates after common commercial soldering processes are typically faster than the rate that would permit complete transformation under such equilibrium conditions. In this paper the authors report a study of the effect of cooling rates on Cu_6Sn_5 crystals. Cooling rates from 200°C ranged from 10°C/minute to 100°C/minute and the effect of isothermal ageing at intermediate temperatures was also studied. The extent of the phase transformation after each regime was determined using synchrotron X-ray diffraction. The findings have important implications for the manufacture of solder joints and their in-service performance.

Introduction
It is becoming increasingly apparent that the reliability of lead-free solder joints is not as consistent and predictable as that of the tin-lead solders they are replacing. That means that so far it has not been possible to establish for lead-free solders the acceleration factors in which designers can have as much confidence as they have in those developed for tin-lead solder. There are many reasons why the behaviour of lead-free solders is less predictable. Lead has a number of effects that served to moderate the behaviour of the tin. Tin is reactive towards most common substrates tending to form intermetallic compounds which have properties very different from the metals from which they are formed. Lead has no such tendency and appears to reduce the reactivity of tin by dilution. By dissolving in the tin to the extent of up to about 2.5% lead has the effect of increasing both strength and ductility and the physical structure of the tin-lead eutectic with layers of a lead-rich phase interleaved with layers of the tin-rich phase also seems to contribute to the general stability and consistency of its mechanical properties. By contrast neither of the additions to tin used in the most common lead-free solders, copper and silver has any significant solubility in tin and instead both form intermetallic compounds with it. Intermetallic compounds tend to have low ductility and can so provide a low energy path for crack propagation. The role of intermetallics in lead-free solders has been further complicated by the realisation that one of the most common, Cu_6Sn_5 undergoes at least one polymorphic transformation over the temperature range to which it is exposed in normal assembly and service.

A phase change can have various consequences for the solder joint. The primary effect is the change in properties of the intermetallic as the crystal structure changes but it has been proposed [1] that the stresses generated by the change in volume that accompanies the transformation could result in the *in situ* fracture of the intermetallic. Such fracture has been reported with the observation that it does not occur at all or to the same extent when Ni has substituted for some of the Cu in the Cu_6Sn_5 [2] (Figure 1). It is expected that such cracking would have negative consequences for the reliability of the joint, particularly under conditions of impact loading and some evidence for that effect has been reported [3].

In this paper ongoing studies of the stability and thermal expansion of the Cu_6Sn_5 intermetallic are reported, including the reproduction of some significant recently published results.[4, 5] Thermal expansion of Cu_6Sn_5, with and without partial substitution of the copper by nickel, was measured by dilatometry and x-ray diffraction. The conditions under which such volume changes might occur in Sn-Cu solder joints has been determined by monitoring by x-ray diffraction the crystal structure of Cu_6Sn_5 during a sequence of rapid cooling and isothermal ageing.

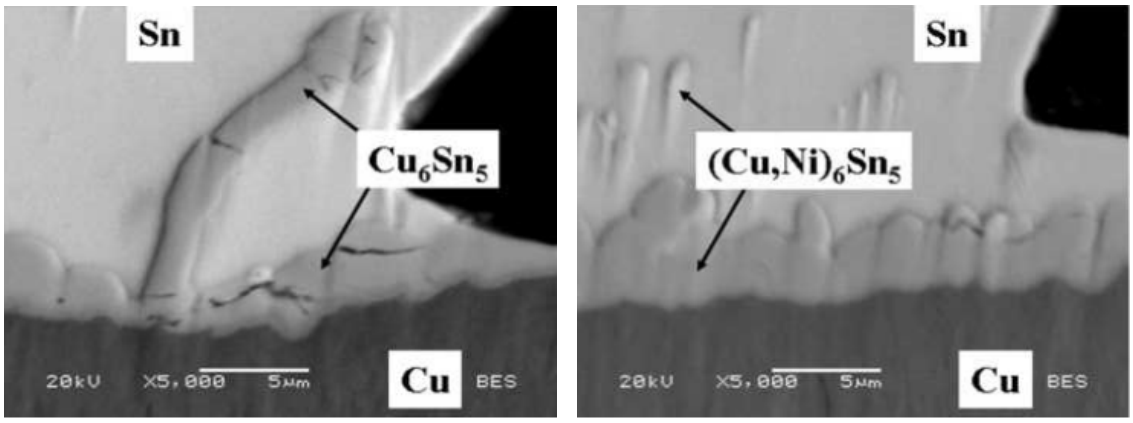


Figure 1. Cracking in the Cu_6Sn_5 at the interface between copper and an Sn-0.7Cu solder sphere. Cracking does not occur with an Sn-0.7Cu-0.05Ni solder sphere when Ni partially substitutes for Cu in the intermetallic[2].

Measuring Thermal Expansion

Dilatometry

Cu_6Sn_5 and $(Cu,Ni)_6Sn_5$ powders were extracted from Sn-4Cu and Sn-4Cu-0.05Ni ingots by dissolution of the tin matrix in an ortho-nitrophenol/sodium hydroxide solution and crushed in agate mortar. The powder was pressed into a rod shape in a 10mm diameter die and linear thermal expansion measured with a NETZSCH 402-C dilatometer. The sample was taken through three cycles from 25°C to 250°C at a rate of 1°C/minute with a 30 minute dwell at each end of each cycle. During the first cycle the powder is compacted so only measurements from the second and third cycle were analysed using the NETZSCH Proteus software. Hexagonal (101) pole figures of the Cu_6Sn_5 and (Cu, $Ni)_6Sn_5$ dilatometry sample rods indicated no particular orientation so that the data collected is taken as representing an average result for what are anisotropic crystals.

Results

Dilation % and the rate of dilation during heating are plotted in Figure 2. The overlapping of the plots from the second and third cycles indicates a high level of reproducibility. The coincidence of the plots for the stabilized and unstabilized IMC at lower temperature indicates that the average coefficients of thermal expansion for both phases are similar. However as the 186°C transformation temperature is approached the rate of dilation of the unstabilized IMC accelerates.

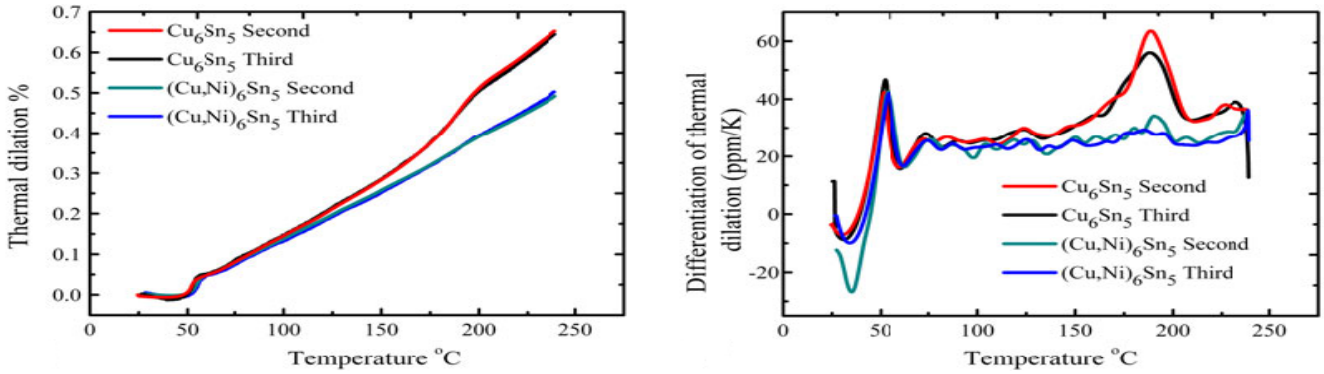


Figure 2. Normalized dilation and dilation rate for unstabilized and Ni-stabilized Cu_6Sn_5 during heating[4].

X-Ray Diffraction

XRD measurements were made on the powder diffraction beam line of the Australian Synchrotron. Powder was loaded into a 0.3mm diameter quartz capillary cell and on the stage heated with hot air at a rate of 6°C/minute to 30, 170, 200, 220 and 250°C. On reaching the desired temperature the sample was held for 1 minute for thermal stabilization and measurements taken for 10 minutes at 2θ scan angles of 10° to 80°. A wave length of 0.0825 nm was used with Cu_6Sn_5 and 0.0773 nm with $(Cu,Ni)_6Sn_5$. Lattice parameters and unit cell volumes were calculated using REITAN-FP analysis software[6] with the refinement parameters optimized to minimize the residual R_{wp}, R_p and S factors. As a reference crystallography and atomic coordination International Centre for Diffraction Data 045-1488 was used for monoclinic and 047-1575 for hexagonal in association with the REITAN-FP.

Results

The disappearance of the minor peaks associated with the monoclinic phase in the unstabilized Cu_6Sn_5 between the x-ray diffraction peak profiles taken at 170°C and 200°C (Figure 3(a)) can be taken as confirmation that somewhere between these two temperature the monoclinic η' form undergoes polymorphic transformation to the hexagonal η form. The x-ray diffraction peak profile indicates that the $(Cu,Ni)_6Sn_5$ retains an hexagonal form throughout that range.

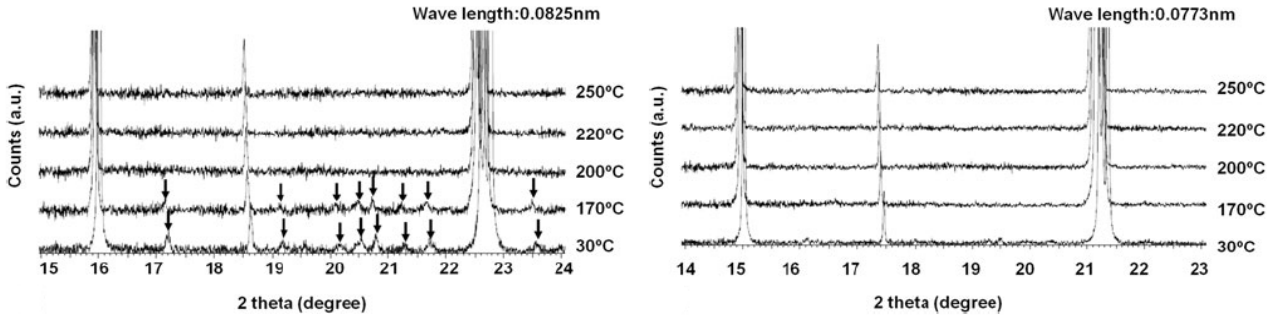
While the incorporation of Ni into the Cu_6Sn_5 structure appears to have no significant effect on the *c* axis lattice parameter it reduces the a axis parameter (Figure 4) and consequently the cell volume (Figure 5)

Transformation Kinetics Studies

Samples similar to those used in the thermal expansion study were subjected to two types of thermal treatment while on the powder beamline of the Australian synchrotron.

Cooling

Measurements at 200°C for 5 minutes were followed by cooling to 50°C at rates of 100, 50, 30, 20, and 10°C min^{-1} and then 5 minutes of measurements at 50°C (Figure 6).



(a) Cu_6Sn_5 (b) $(Cu, Ni)_6Sn_5$

Figure 3. X-ray diffraction peak profile for IMC samples heated from 30°C to 250°C[4]

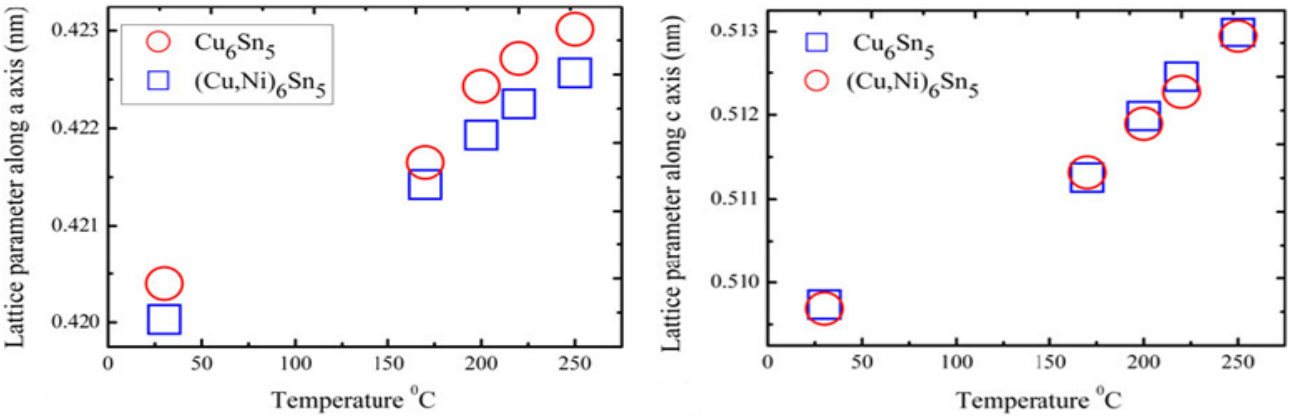


Figure 4. *a* and *c* axis lattice parameters in hexagonal Cu_6Sn_5 and $(Cu,Ni)_6Sn_5$ as a function of temperature.[4]

Cooling Plus Isothermal Ageing

Measurements at 200°C for 5 minutes followed by cooling at a rate of 100°C min^{-1} to 180, 160, 150, 140, and 100°C followed by 5 minutes of data collection at each of these temperatures for up to 12 measurements (Figure 7). Measurements of the unstabilized Cu_6Sn_5 were continued until complete conversion to the monoclinic form had occurred and measurements over a similar time frame were made for the stabilized $(Cu,Ni)_6Sn_5$.

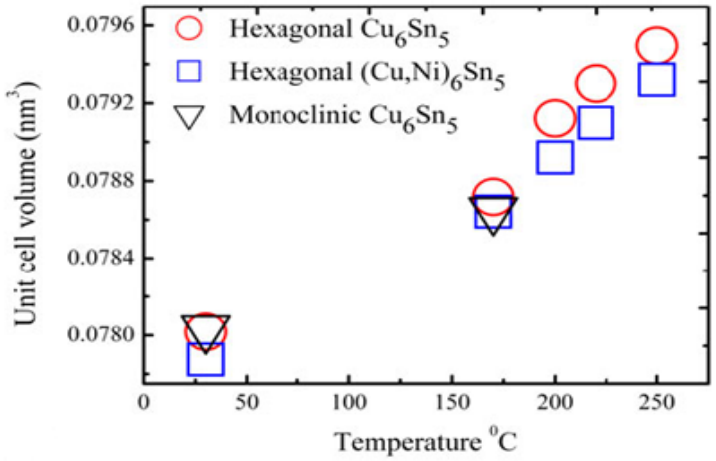


Figure 5. Unit cell volumes as a function of temperature.[4]

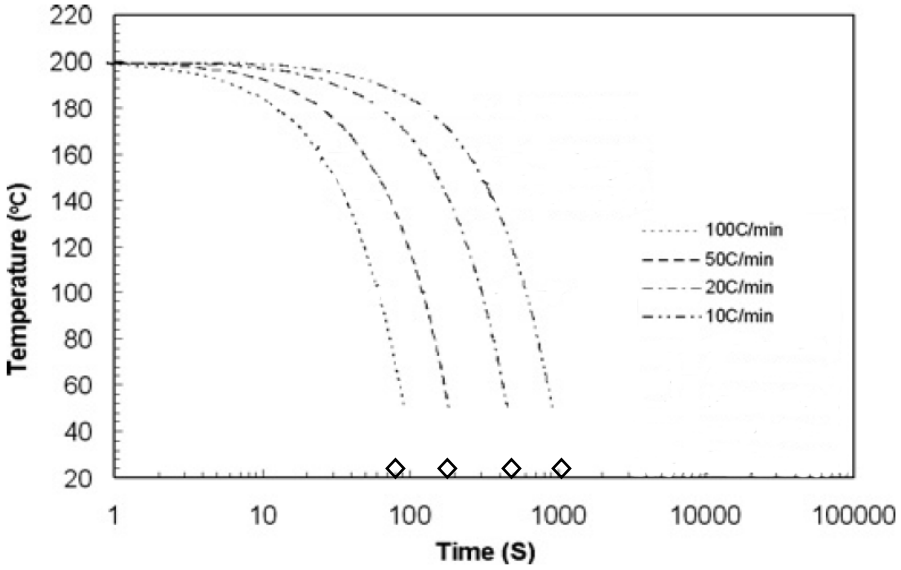


Figure 6. Cooling profiles to which samples of Cu_6Sn_5 and $(Cu,Ni)_6Sn_5$ were subjected.[5]

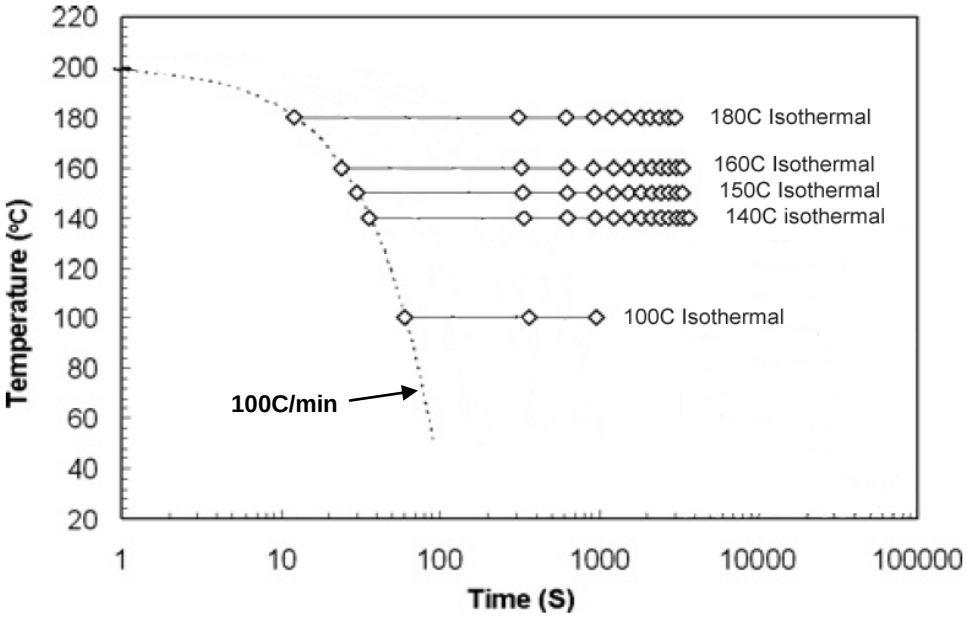


Figure 7. Cooling and isothermal ageing profiles to which samples of Cu_6Sn_5 and $(Cu,Ni)_6Sn_5$ were subjected.[5]

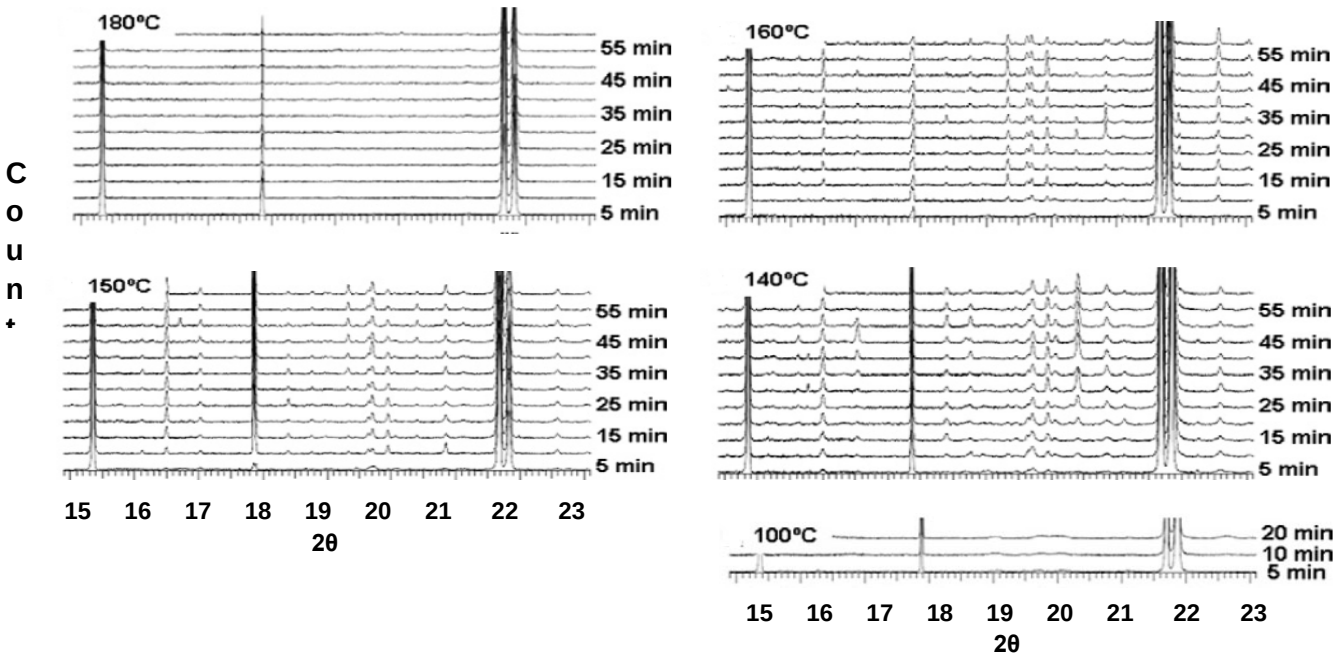


Figure 8. X-ray diffraction peak profiles for Cu_6Sn_5 samples from isothermal ageing experment.[5]

Results

From the peak profiles in Figure 8 it can be seen that for the samples of the unstabilized Cu_6Sn_5 cooled at 100°Cmin^{-1} and aged at temperatures of 160, 150 and 140°C transformation to the monoclinic form (revealed by the appearance of minor peaks) begins almost immediately. At 180°C the hexagonal form is retained and in the samples cooled to 100°C a metastable hexagonal phase is retained. Figure 9 shows the summarised results of the XRD measurements for both the continuously cooled and isothermally held samples.

Discussion

Taking into account the results presented in Figures 8 and 9 a TTT diagram has been constructed as illustrated in Figure 10. This provides a means of predicting the phases likely to be present as a function of the thermal profile to which the solder is subjected. The times at which the transformation is completed are yet to be finally determined (dashed line).

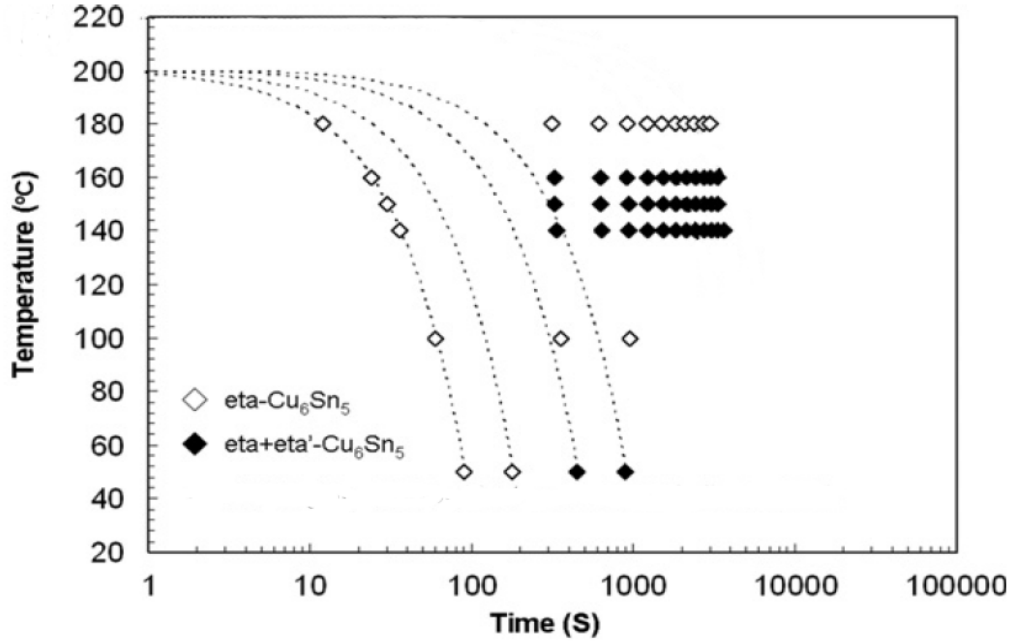


Figure 9. Phase constitution of Cu_6Sn_5 after cooling rate and isothermal ageing[5]

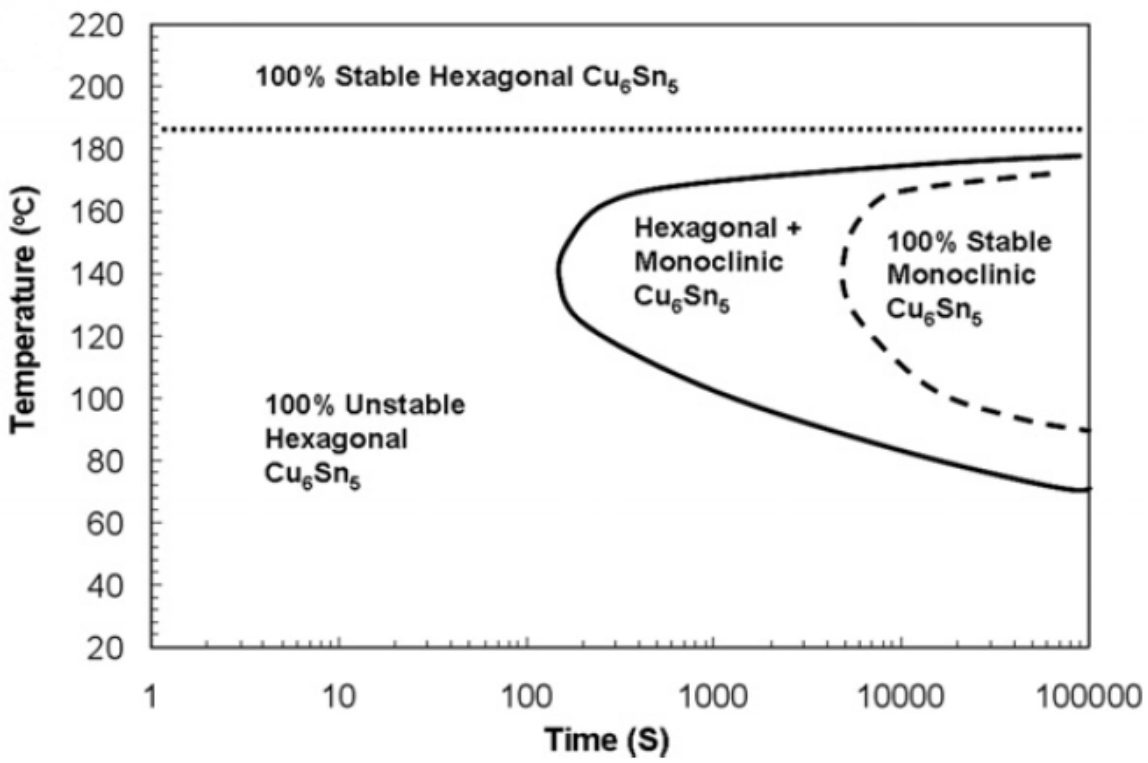


Figure 10. Estimated boundaries of Temperature-Time-Transformation (TTT) curves for Cu_6Sn_5.[5]

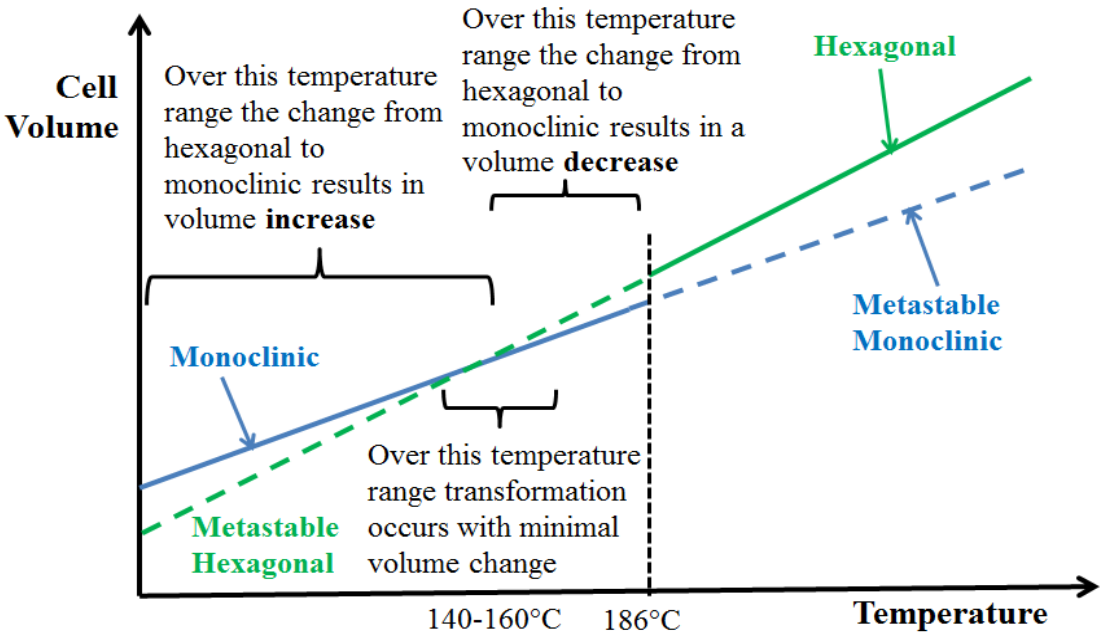


Figure 11. Hypothetical plot illustrating a possible technique for minimizing the stress generated by the η→η' transformation

Based on the dilatometry measurements and the study of the polymorphic transformation under different thermal profiles a concept for risk minimization is being proposed that is illustrated schematically in Figure 11. On the basis that a volume change in either direction that accompanies the polymorphic transformation could generate stress that could trigger joint

cracking it is proposed that in alloys that do not have the benefit of a Cu_6Sn_5 phase that has been stabilized by Ni the cooling be managed to provide an opportunity for the transformation to occur at a temperature at which the change in unit cell volume is at a minimum.

Conclusions

- In dilatometry studies the transformation from monoclinic η' to the hexagonal η phase during heating can be observed as an expansion over a temperature range around the nominal 186°C transformation temperature.
- Cu_6Sn_5 with partial substitution of Cu by Ni retains its hexagonal crystal form over the range room temperature to 250°C.
- The partial substitution of Cu by Ni in the hexagonal Cu_6Sn_5 crystal reduces the lattice parameter in the *a* direction but does not significantly affect the lattice parameter in the *c* direction.
- At cooling rates as slow at 50°Cmin^{-1} metastable hexagonal η phase can be retained to 50°C.
- In isothermal interruptions to 100°Cmin^{-1} cooling at 160, 150 and 140°C transformation from the metastable hexagonal phase to the monoclinic phase has begun by 400 seconds. At 180°C the transformation did not begin within an hour. At 100°C the metastable hexagonal η phase remained unchanged for up to 1000 seconds.
- On the basis of the results of rapid cooling and isothermal ageing experiments it is possible to start to map a temperature-time-transformation ("TTT") diagram for the η→η' transformation in Cu_6Sn_5.
- On the basis of a presumption that the different coefficients of thermal expansion of the hexagonal η phase and the monoclinic η' phase can be extrapolated into the temperature ranges where the phases are metastable it is hypothesized that whether the change from metastable η' to η is associated with an expansion or contraction depends on the temperature at which it occurs. That creates an opportunity for minimizing potential damage to the joint integrity by allowing the transformation to occur at a temperature at which the difference in coefficient of thermal expansion is close to zero.

Acknowledgements

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References

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[2] K. Nogita, Intermetallics 18, (2010) 145-149.

[3] H. Tsukamoto, T. Nishimura, S. Suenaga, S. D. McDonald, K. W. Sweatman, K. Nogita, Microelectronics Reliability (2011).

[4] D. Mu, J. Read, Y.-F. Yang, K. Nogita, Journal of Materials Research 26, 20 (2011) 2660 - 2664.

[5] K. Nogita, C. M. Gourlay, S. D. McDonald, Y. Q. Wu, J. Read, Q. F. Gu, Scripta Materialia 65, (2011) 922-925.

[6] F. Izumi, K. Momma, Solid State Phenomena 130, (2007) 15-20.

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Stuart McDonald & Kazuhiro Nogita — **University of Queensland Australia**

your partner for soldering solution

NIHON SUPERIOR

THE UNIVERSITY OF QUEENSLAND
AUSTRALIA

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by:

- Dekui Mu
- Jonathan Read
- Dr Stuart McDonald
- Dr Ya Feng Yang
- Dr Yueqin Wu
- Dr Qinfen Gu

And published in the following papers:

- K. Nogita, Intermetallics 18, (2010) 145-149
- H. Tsukamoto, T. Nishimura, S. Suenaga, S. D. McDonald, K. W. Sweatman, K. Nogita, Microelectronics Reliability (2011).
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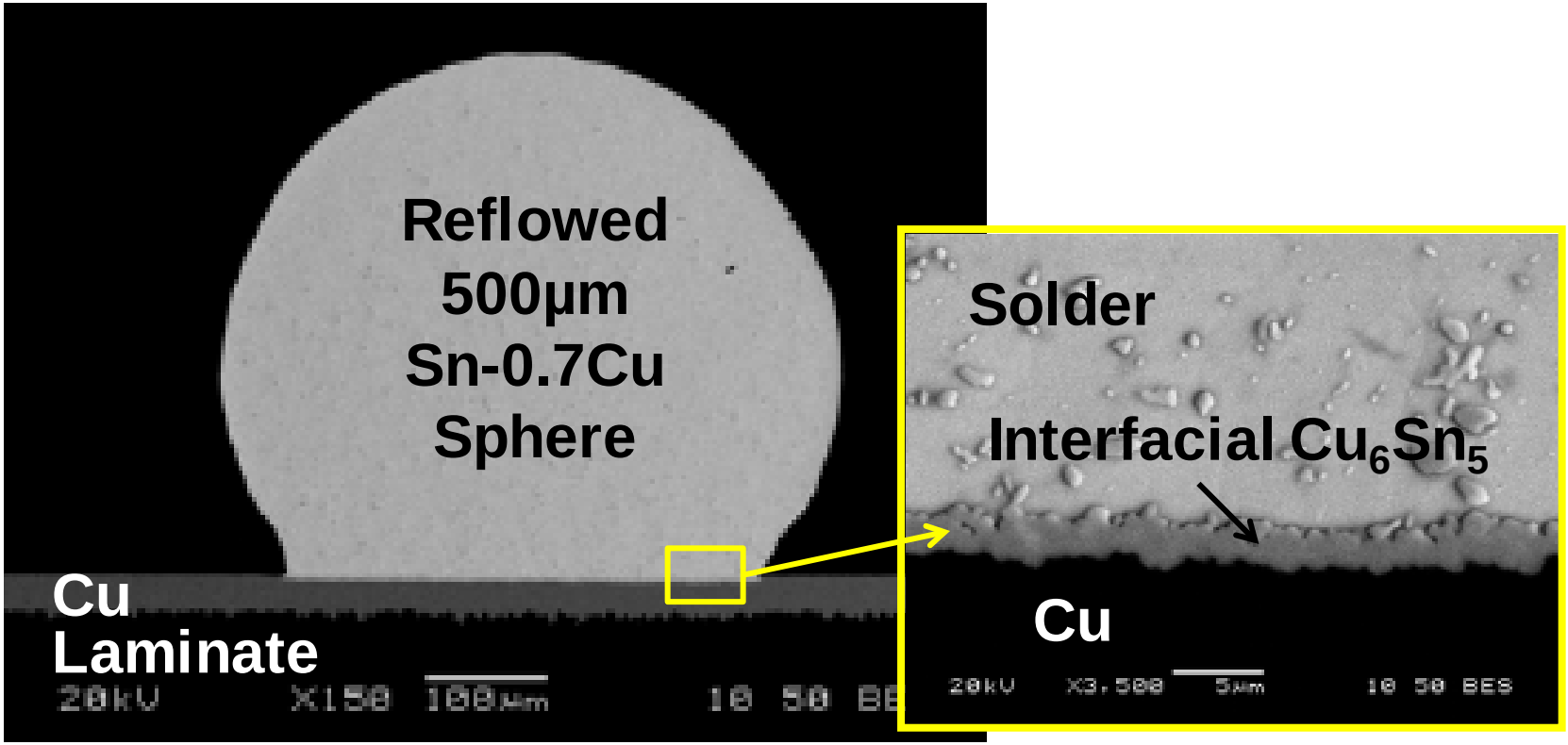
Effect of Cooling Rate on the Intermetallic Layer in Solder Joints

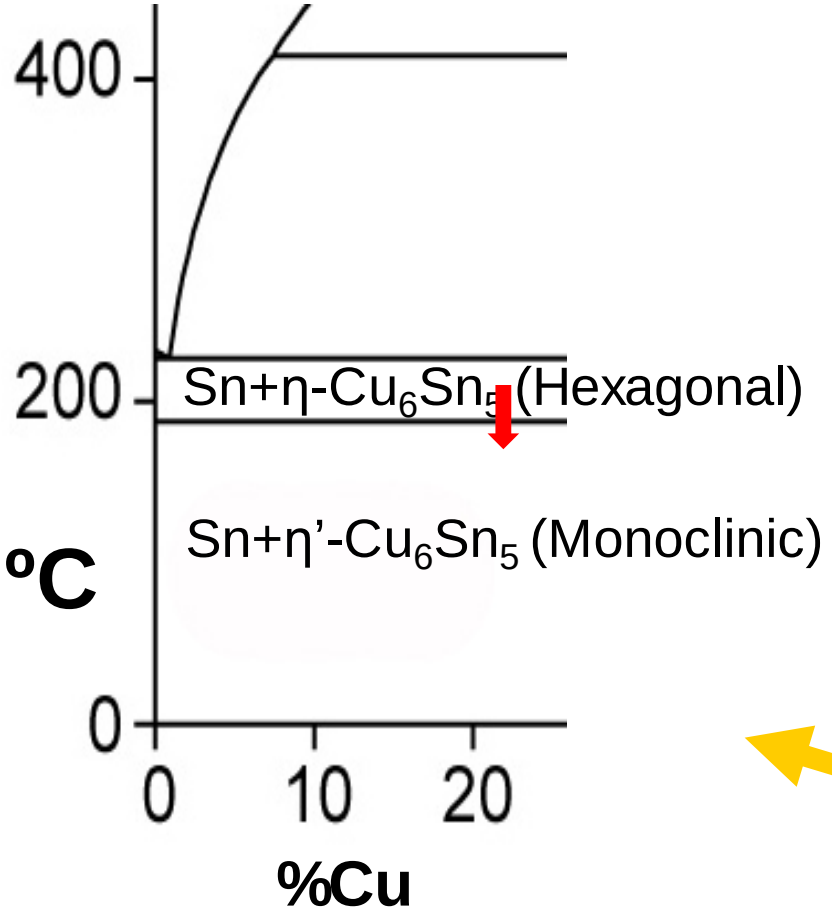
- Cu_6Sn_5 is an important constituent of
  - Most lead-free solder joints
  - All solder joints to copper substrates
- Cu_6Sn_5 undergoes a phase change from an hexagonal to a monoclinic crystal structure over the temperature range between the freezing point of the solder and normal operating temperatures.

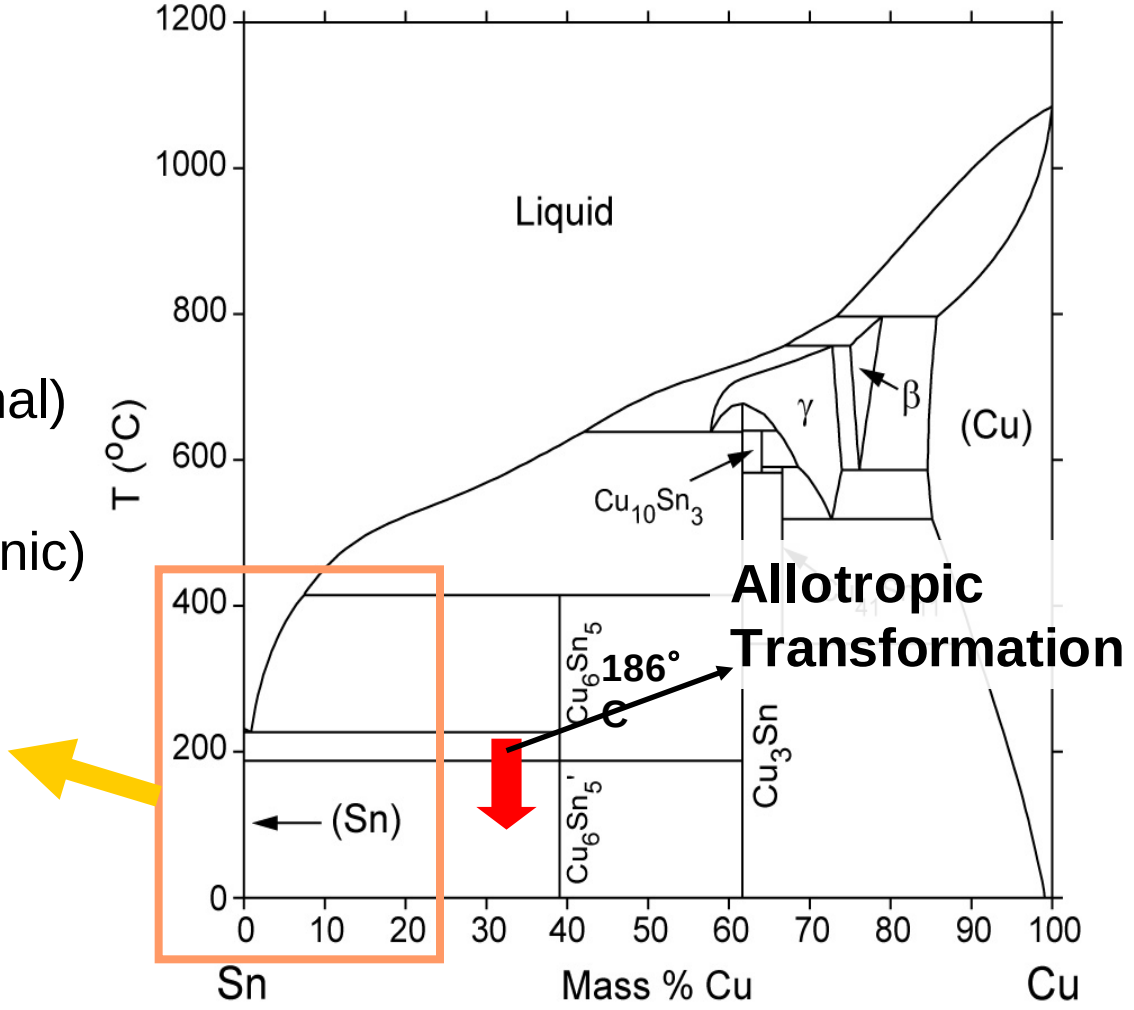
Interfacial Intermetallic

A key part of the microstructure of a solder joint



The Phase Change





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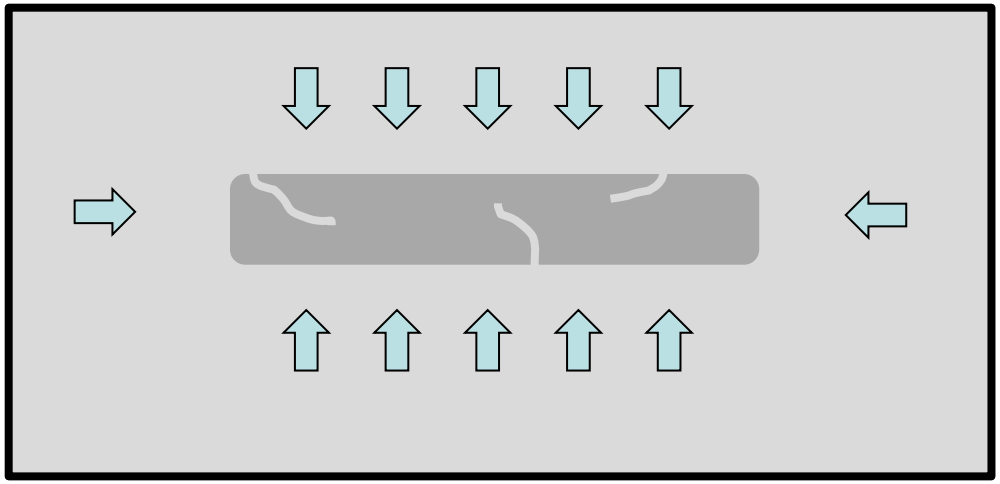
What are the consequences?

What are the Consequences of the Phase Change?

A change in crystal structure → A change in crystal volume

A change in volume in a phase that is constrained in another phase generates a stress



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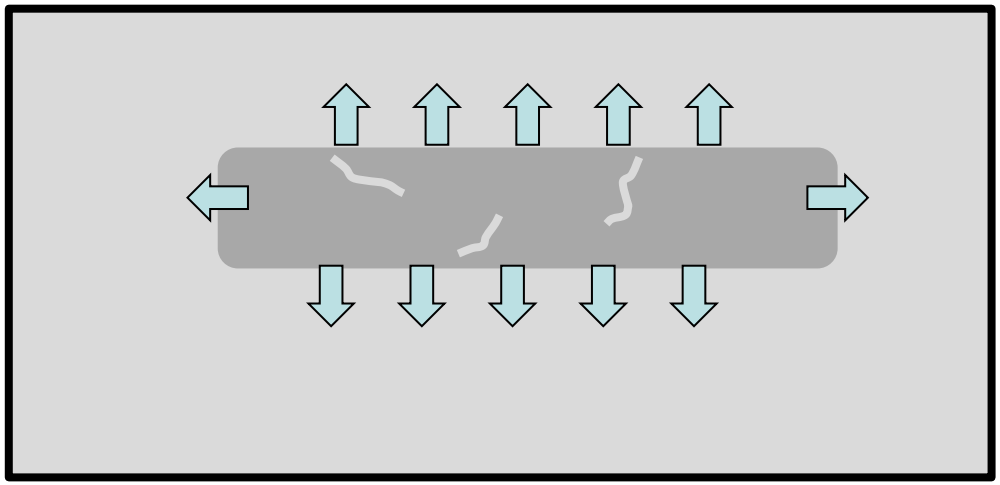

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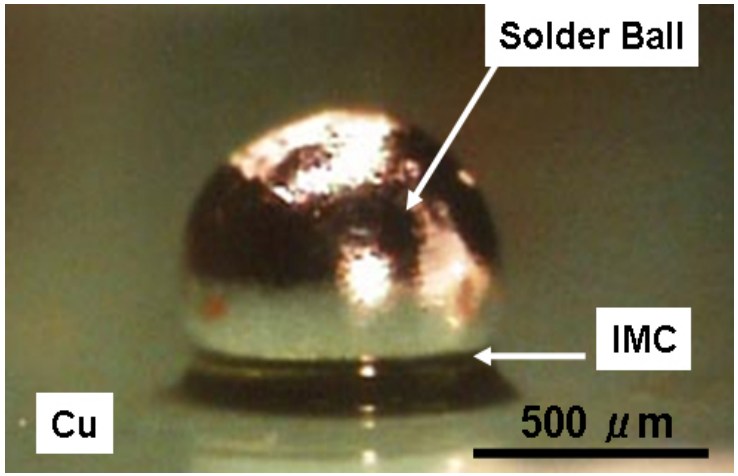
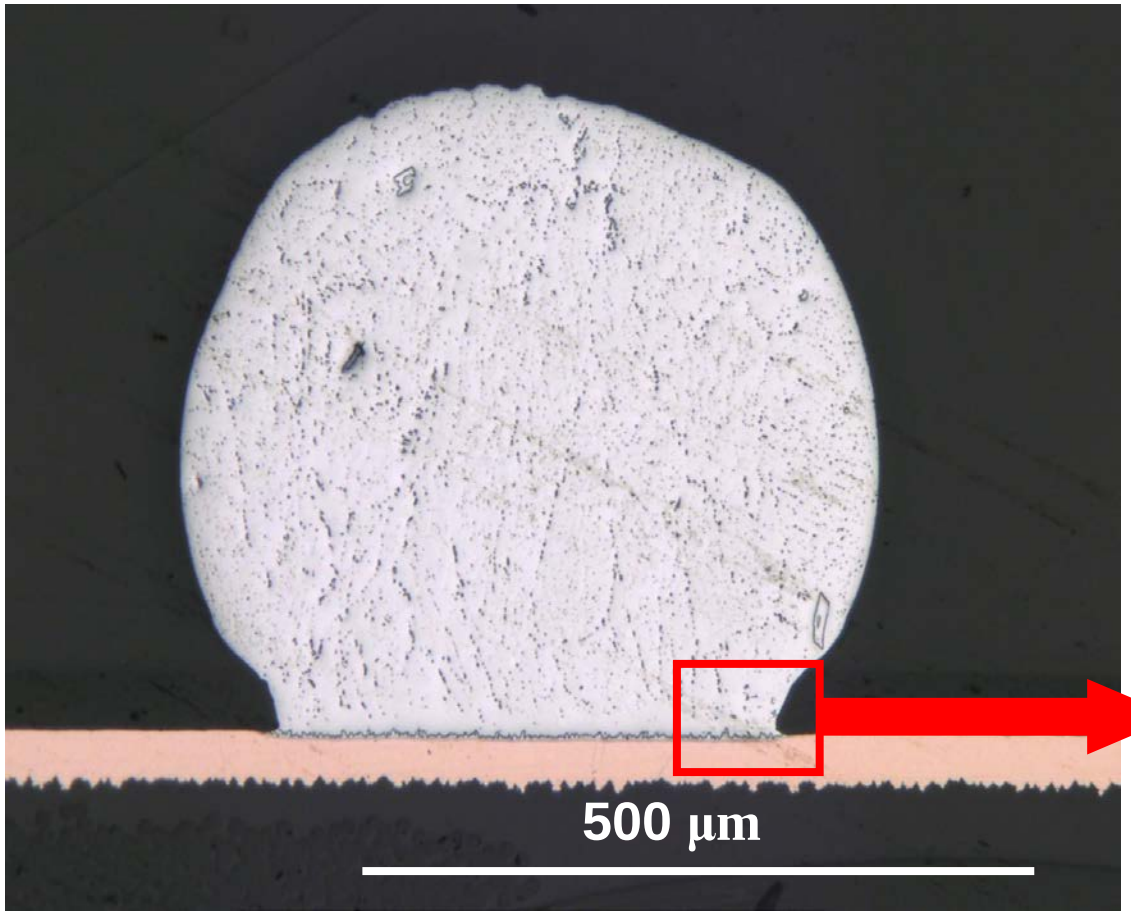
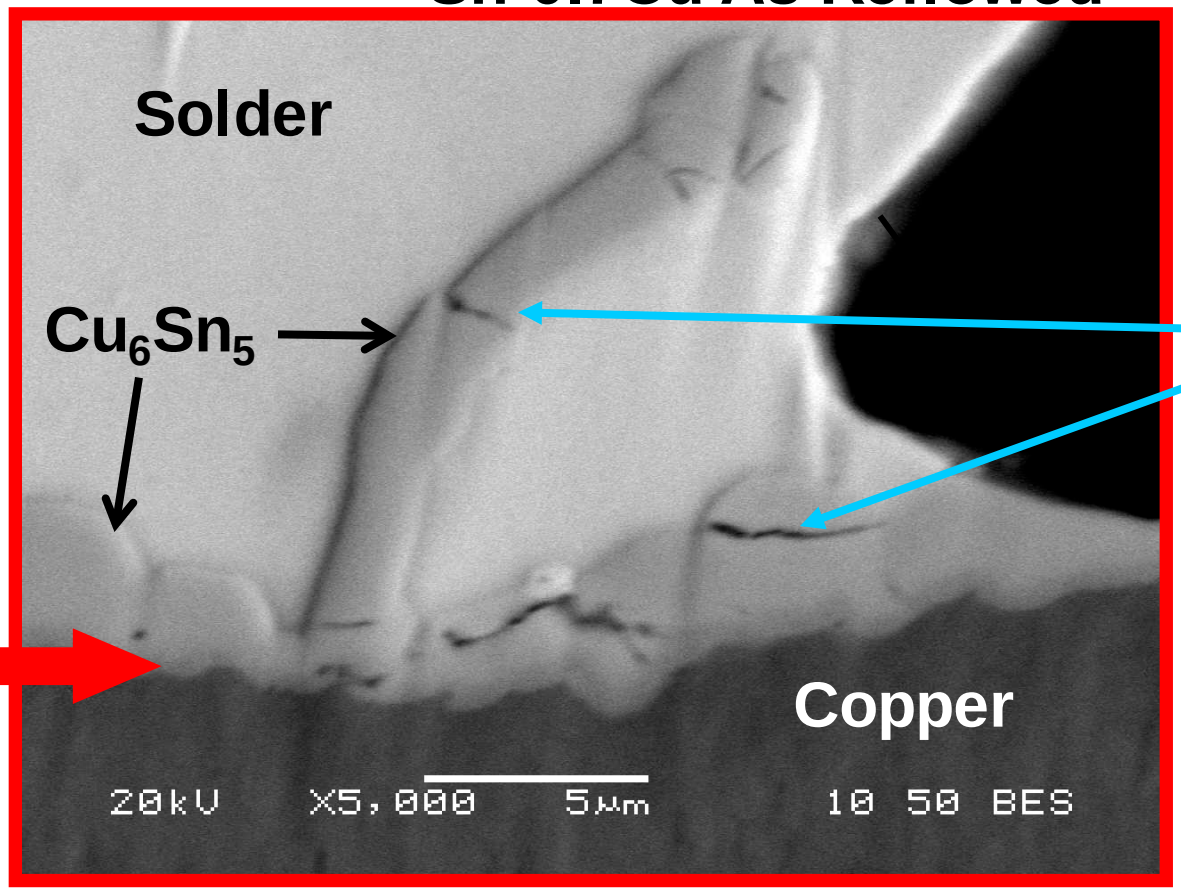




What are the Consequences of the Phase Change?

Sn-0.7Cu As Reflowed

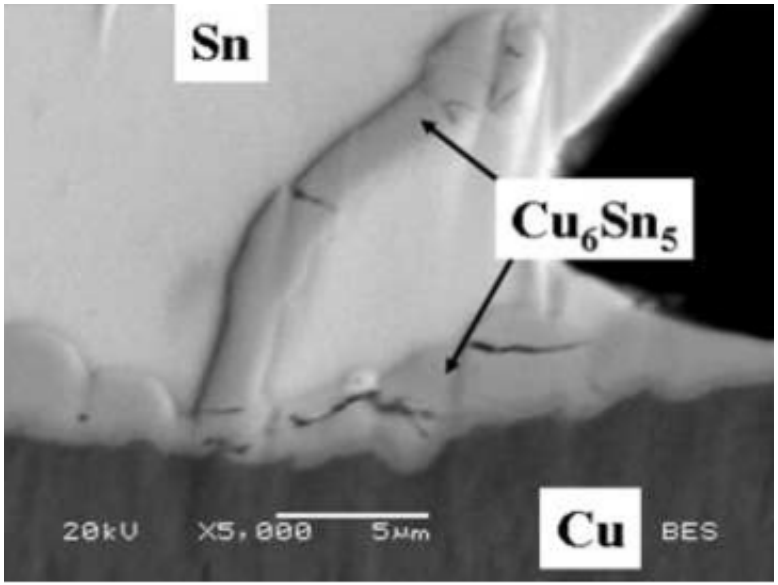


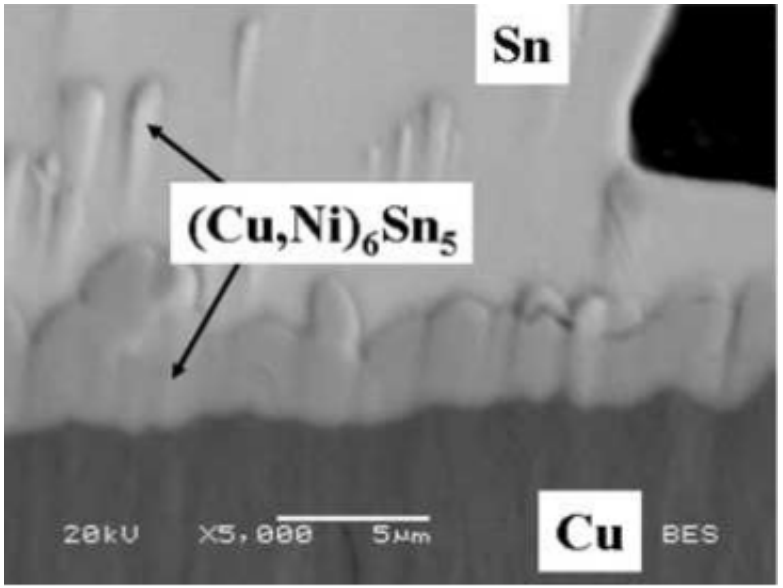
Cracking due to stress generated by volume change η → η'

K. Nogita, Intermetallics 18, (2010) 145-149

The phase change can be prevented by the incorporation of Ni into the alloy

Ni selectively incorporates in the Cu_6Sn_5 and stabilizes the hexagonal phase at temperatures below 186° C.



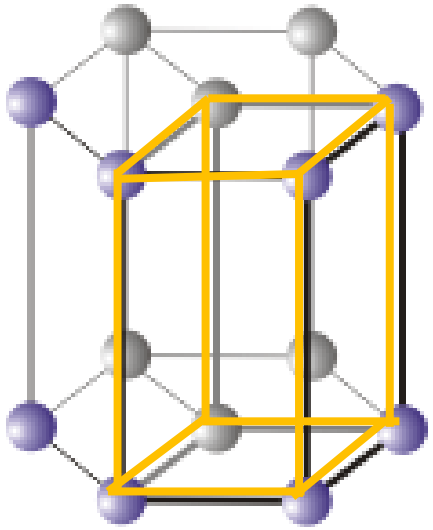


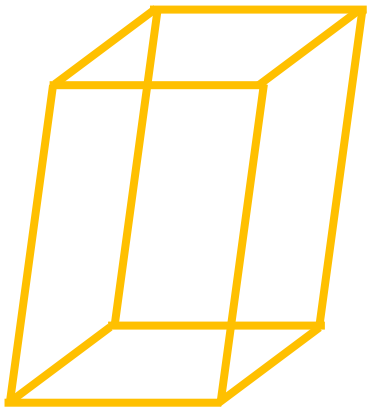
The Question is….

Is there a way of avoiding the potential for cracking in unstabilized Cu_6Sn_5 when it undergoes the transformation from the hexagonal to the monoclinic form?

Can the volume change be minimized?

Find the temperature at which the key lattice dimensions of the *hexagonal* Cu_6Sn_5 are about the same as those of the *monoclinic* Cu_6Sn_5

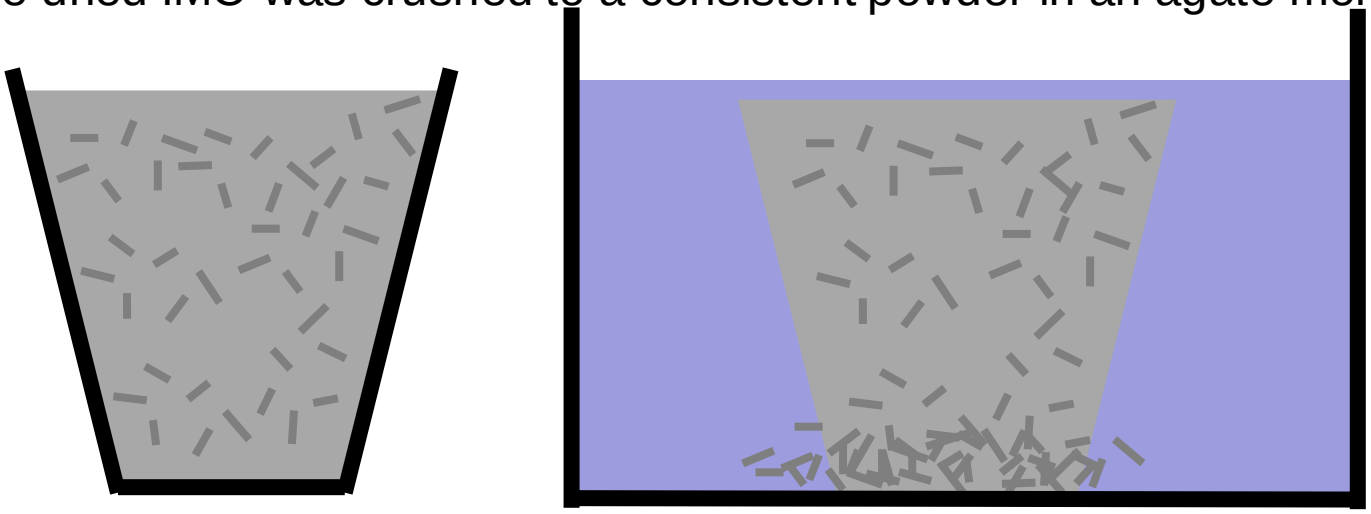




Hexagonal → monoclinic is not a big change.

Measure the expansion of hexagonal and monoclinic Cu_6Sn_5 as a function of temperature

- Ingots of Sn-4Cu an Sn-4Cu-0.05Ni were cast
- Samples of Cu_6Sn_5 and $(Cu,Ni)_6Sn_5$ were obtained by recovering by filtration the crystals left after the tin matrix has been dissolved in a solution of ortho-nitrophenol and NaOH in water.
- The undissolved IMC was rinsed with deionized water then alcohol before being air dried.
- The dried IMC was crushed to a consistent powder in an agate mortar.



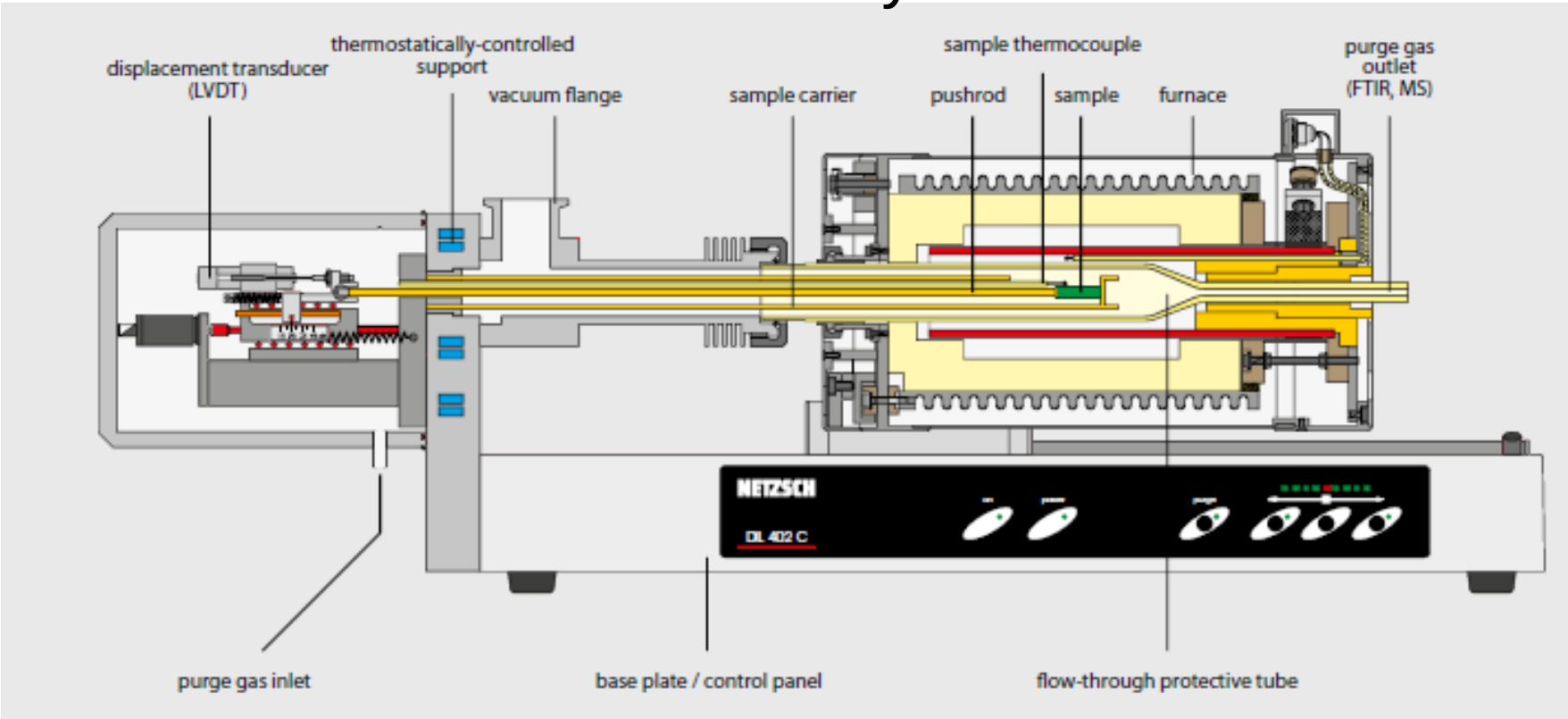
Measuring the Thermal Expansion of Cu_6Sn_5

Dilatometry

Netzsch 402 C Dilatometer

Measuring the Thermal Expansion of Cu_6Sn_5

Dilatometry

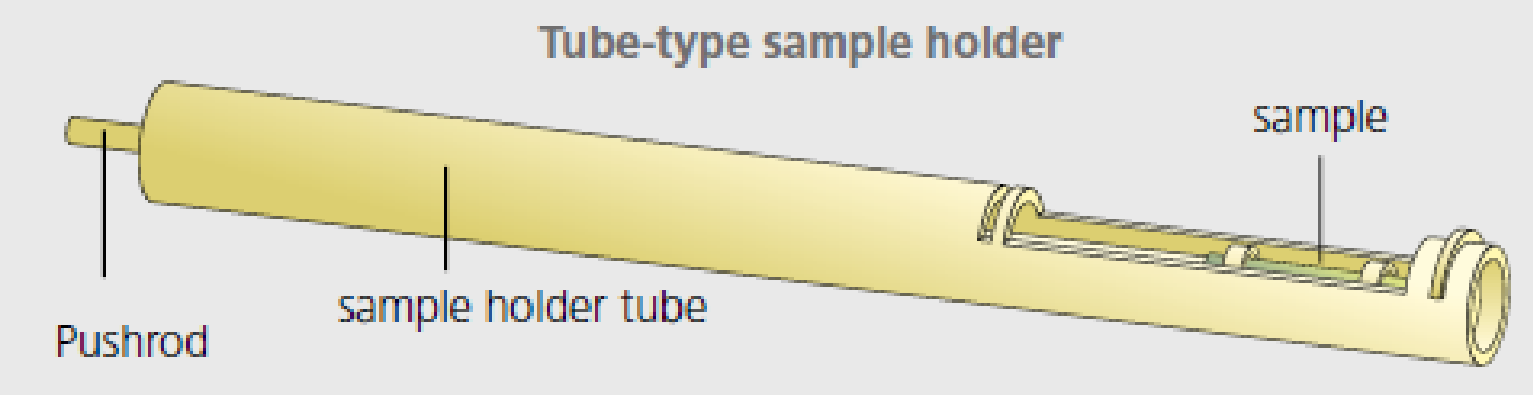


Netzsch 402 C Dilatometer

Measuring the Thermal Expansion of Cu_6Sn_5

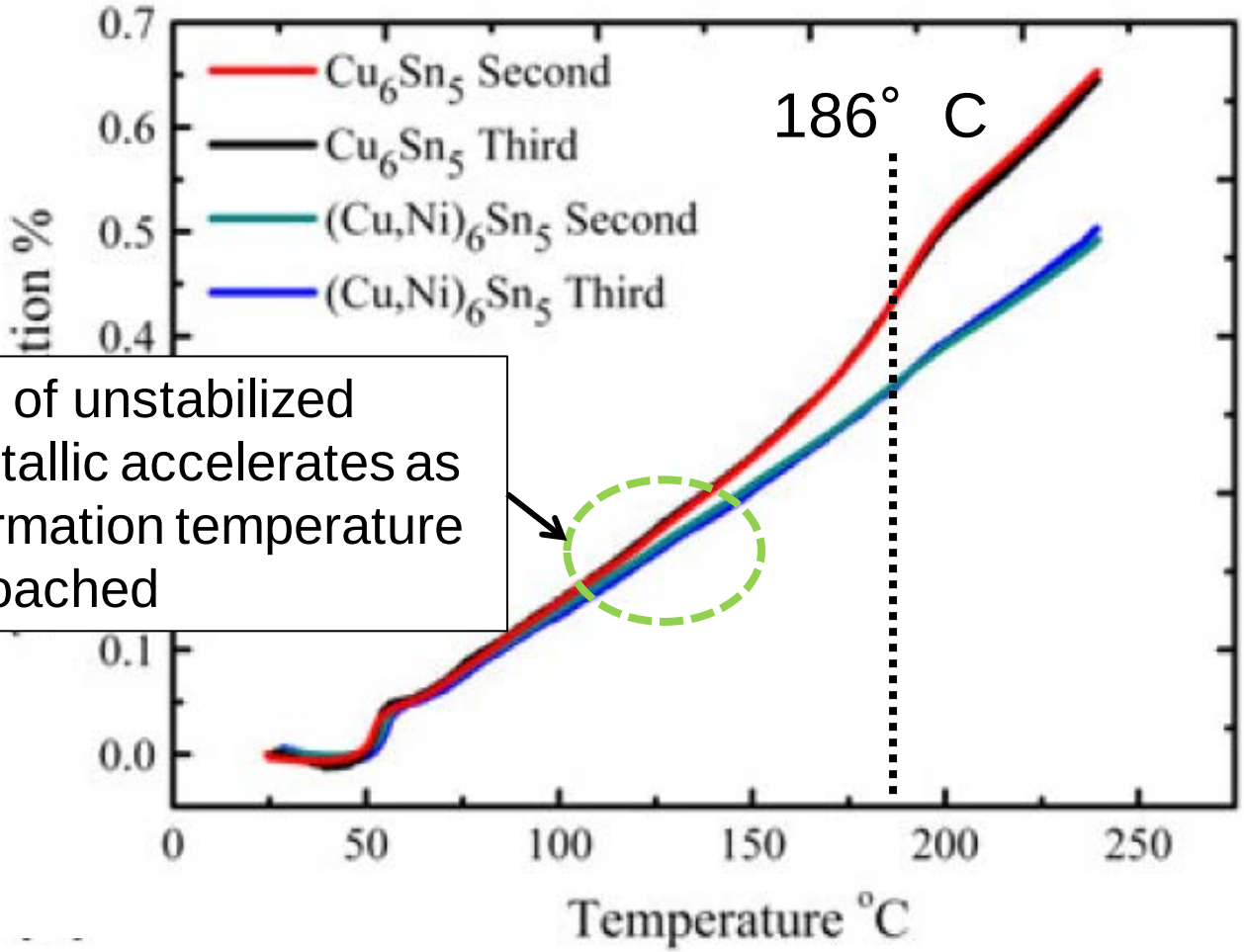
Dilatometry

Crushed IMC pressed into a rod shape in a 10mm diameter die



- Linear thermal expansion measured over the range 25° C – 250° C
- Heating/Cooling rate ≈1° C/minute with 30 minute dwell at the end of each cycle.
- Three cycles.
  - 1st for consolidation
  - 2nd and 3rd used for analysis by Netzsch “Proteus” software

Dilation as a Function of Temperature

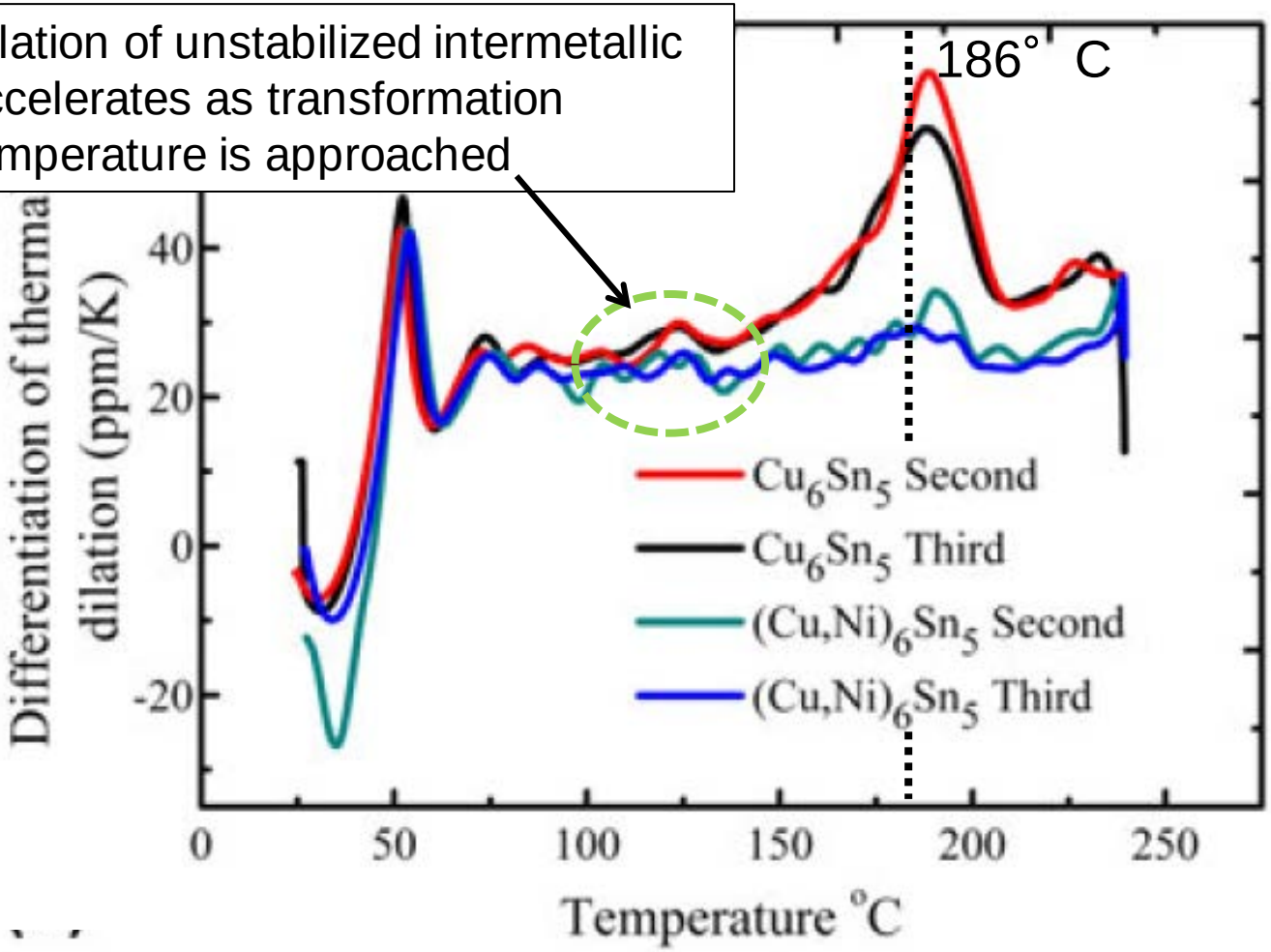


Dilation of unstabilized intermetallic accelerates as transformation temperature is approached

] D. Mu, J. Read, Y.-F. Yang, K. Nogita, Journal of Materials Research 26, 20 (2011) 2660 - 2664.

Dilation as a Function of Temperature

Dilation of unstabilized intermetallic accelerates as transformation temperature is approached



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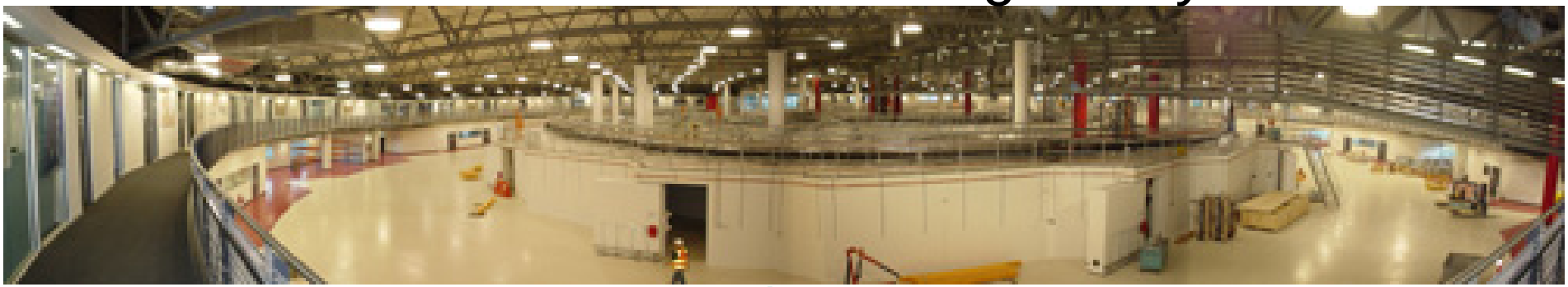
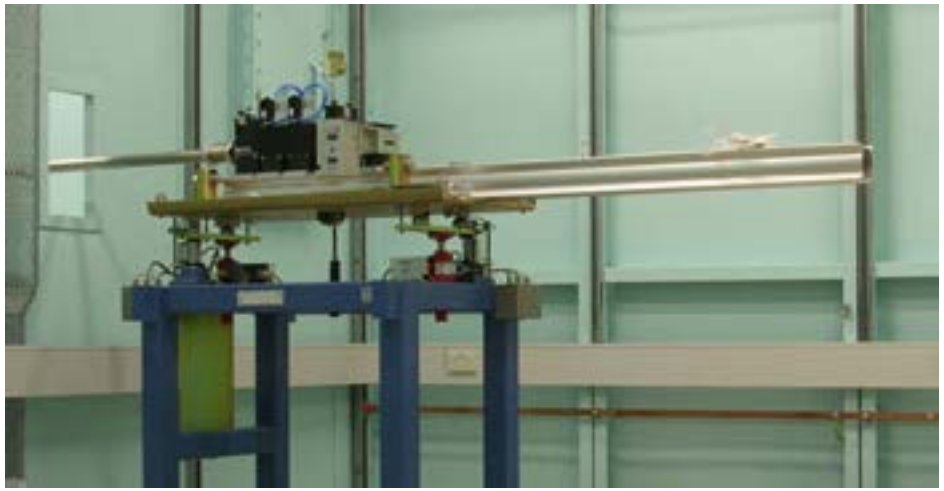
Dilation as a Function of Temperature

Measure Lattice Parameters Using X-Ray Diffraction



www.synchrotron.org.au



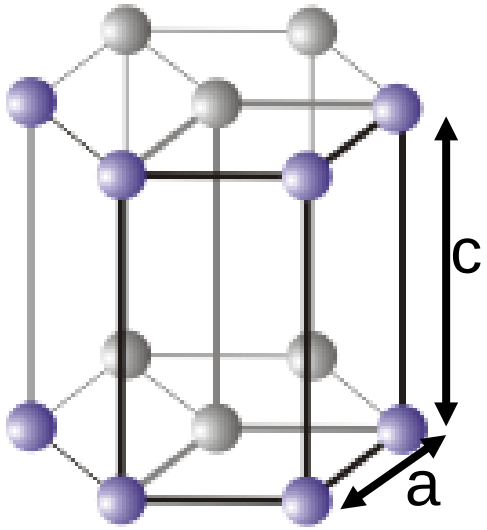
- Synchrotron XRD measurements were done at the Powder Diffraction beam line at the Australian Synchrotron.
- The Cu_6Sn_5 and $(Cu,Ni)_6Sn_5$ powders were loaded into a quartz capillary sample cell (0.3 mm in diameter) and heated with a hot air gun.

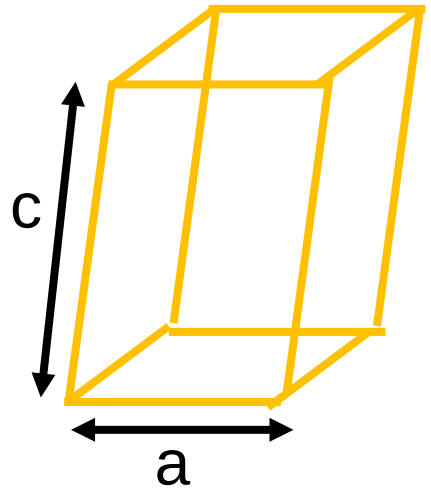
Dilation as a Function of Temperature

Measure Lattice Parameters Using X-Ray Diffraction

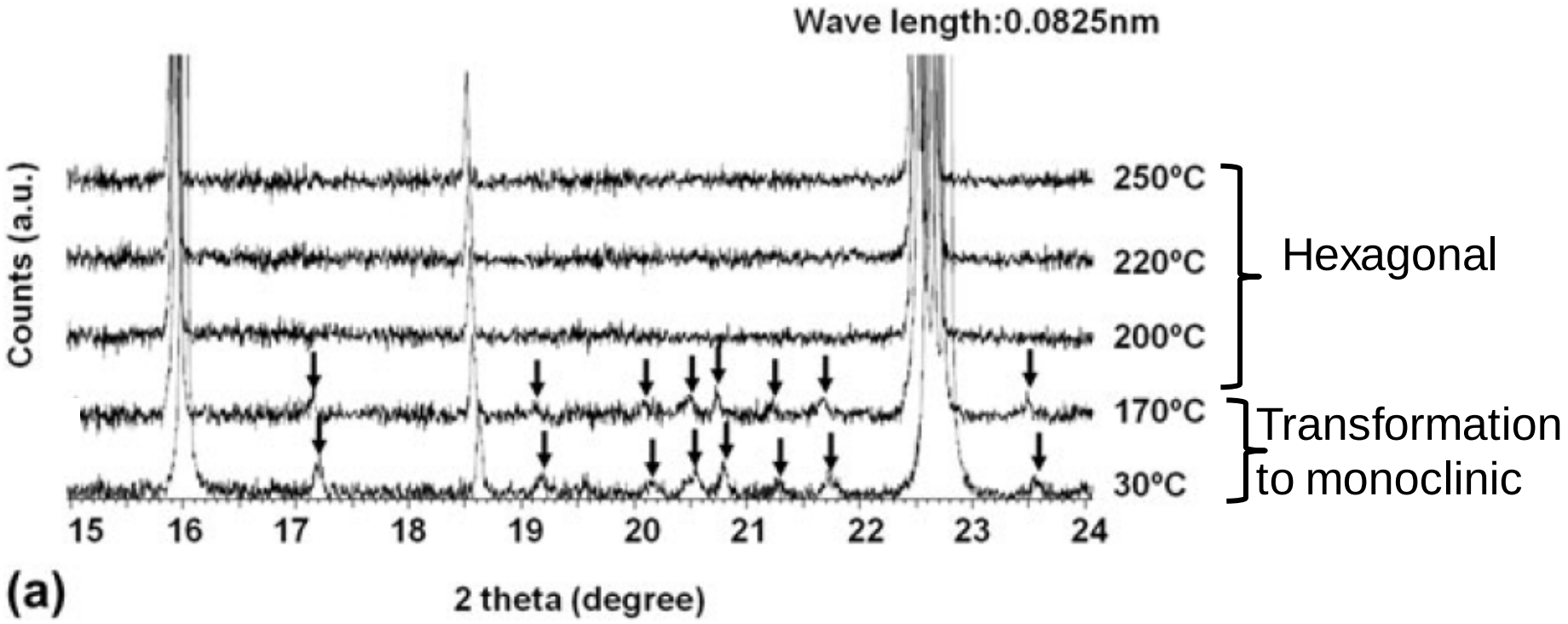
- Synchrotron XRD was performed using 15kV acceleration voltage and 100 to 600 2θ scan angles at temperatures of 30, 170, 200, 220, and 250ºC with heating rate of 6ºC/min.
- Once the desired temperature was reached, the sample was kept at that temperature for eleven minutes, with one minute for thermal stabilisation and ten minutes for data collection.
- The lattice parameters and unit cell volume of Cu_6Sn_5 and $(Cu,Ni)_6Sn_5$ were calculated using X-ray peak data obtained at each temperature using the RIETAN-FP Rietveld analysis software. The refinement parameters were optimized to minimize the residual Rwp, Rp and S factors.
- As a reference crystallography and atomic coordination, ICDD (International Centre for Diffraction Data) number of 045-1488 (for Monoclinic) and 047-1575 (for Hexagonal) were used in association with RIETAN-FP.

Measuring Lattice Parameters





X-Ray Spectrum of Cu_6Sn_5 as a Function of Temperature



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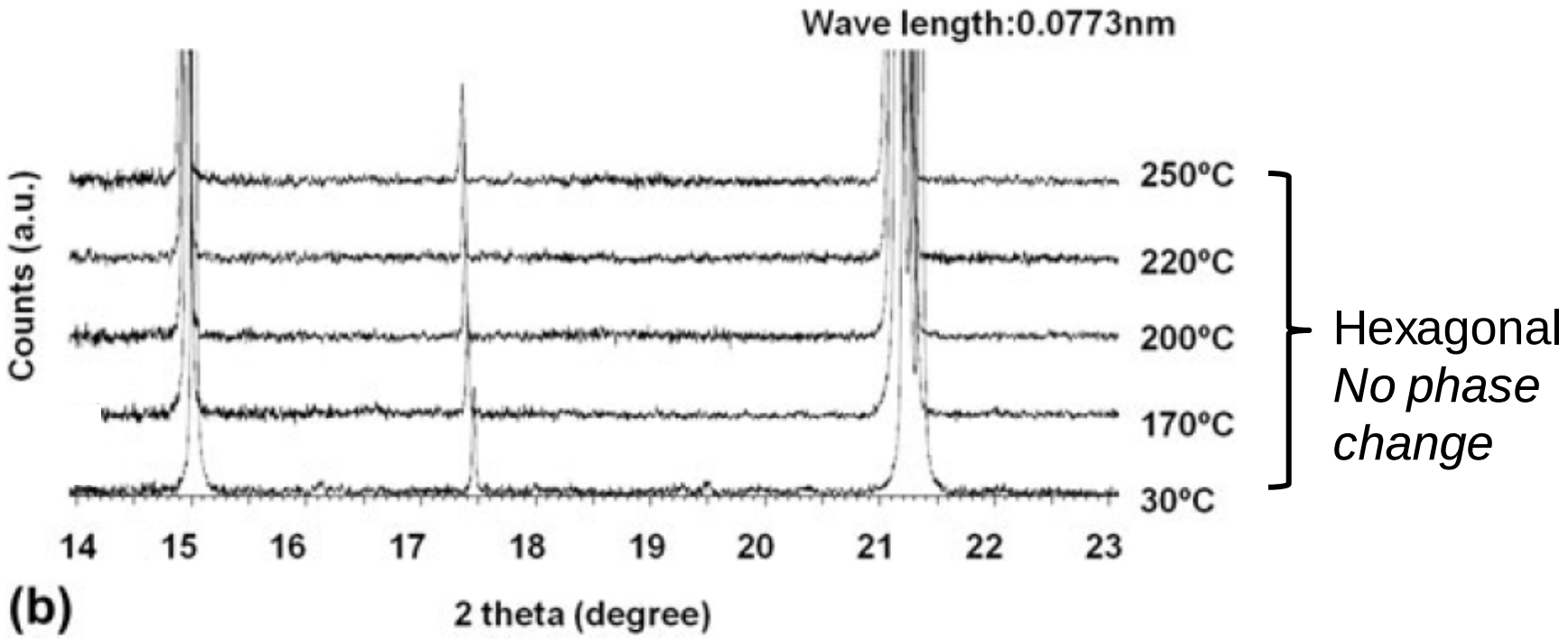
X-Ray Spectrum of $(Cu,Ni)_6Sn_5$ as a Function of Temperature



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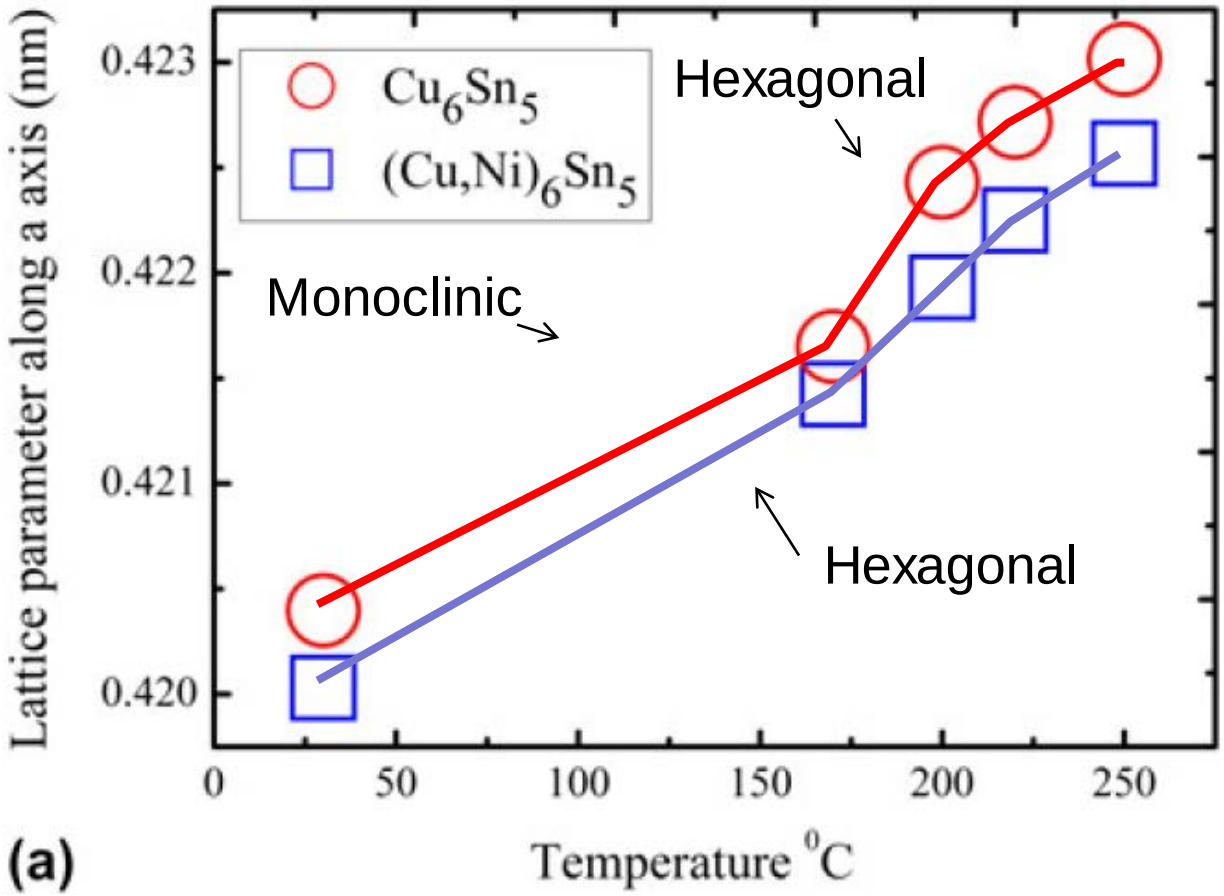
Increase in "a" Axis Lattice Parameter with Temperature



Incorporation of Ni reduces "a" axis lattice dimension.

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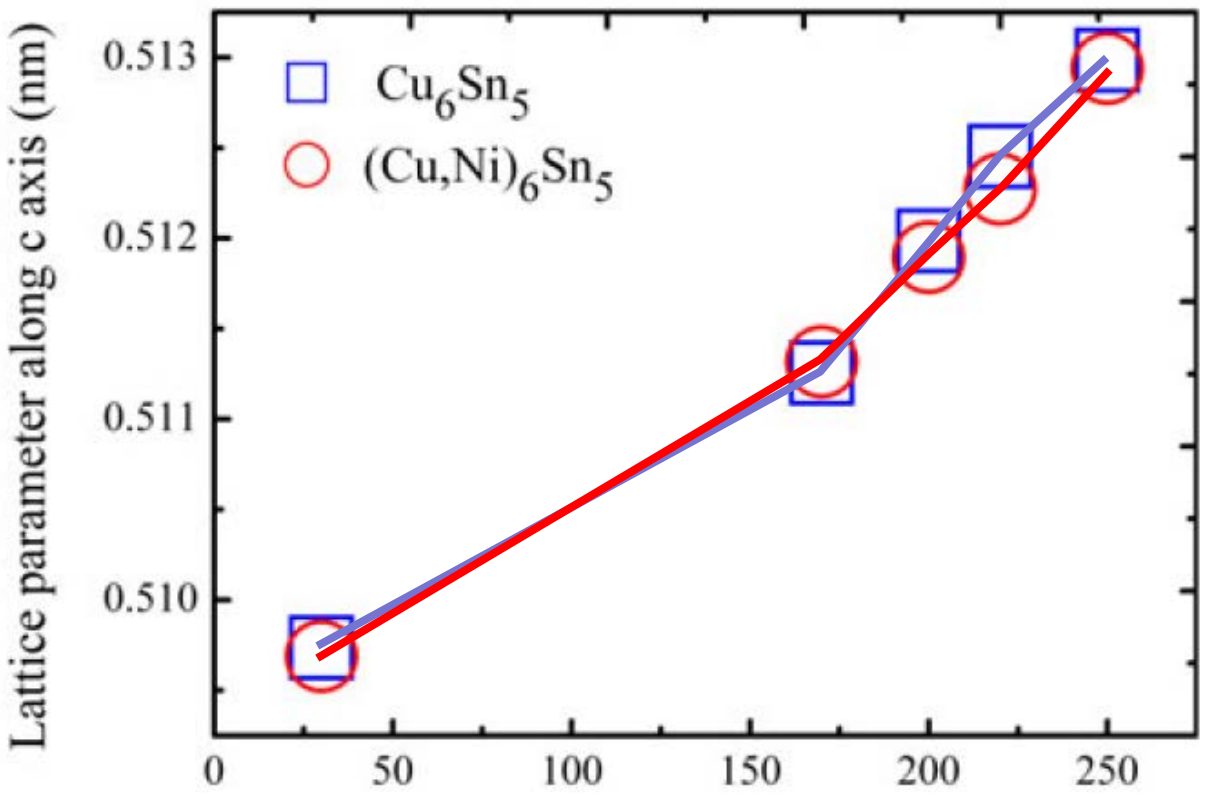
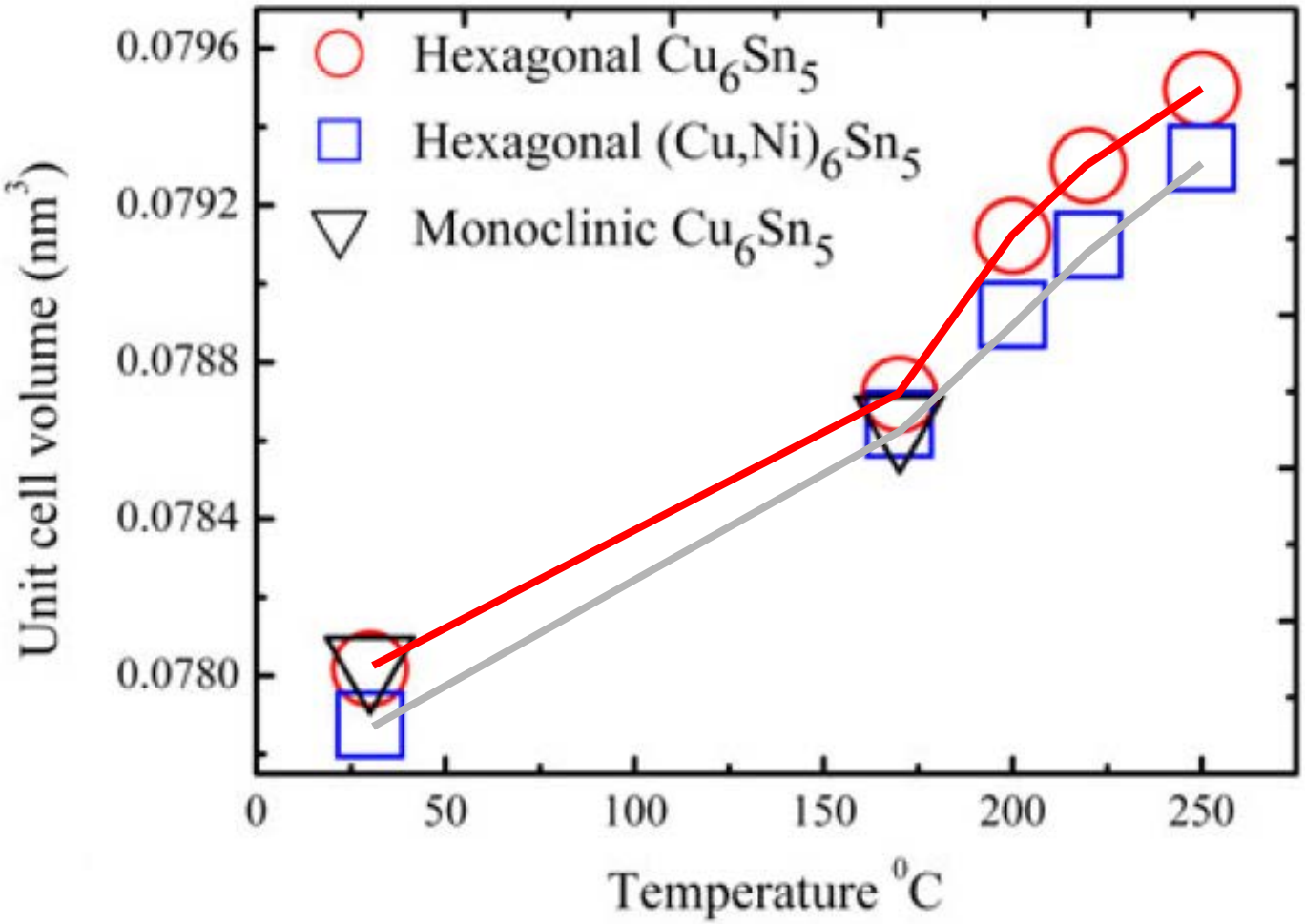
Increase in "c" Axis Lattice Parameter with Temperature



Incorporation of Ni has little effect on "c" axis lattice dimension.

] D. Mu, J. Read, Y.-F. Yang, K. Nogita, Journal of Materials Research 26, 20 (2011) 2660 - 2664.

Increase in Calculated Cell Volume with Temperature



] D. Mu, J. Read, Y.-F. Yang, K. Nogita, Journal of Materials Research 26, 20 (2011) 2660 - 2664.

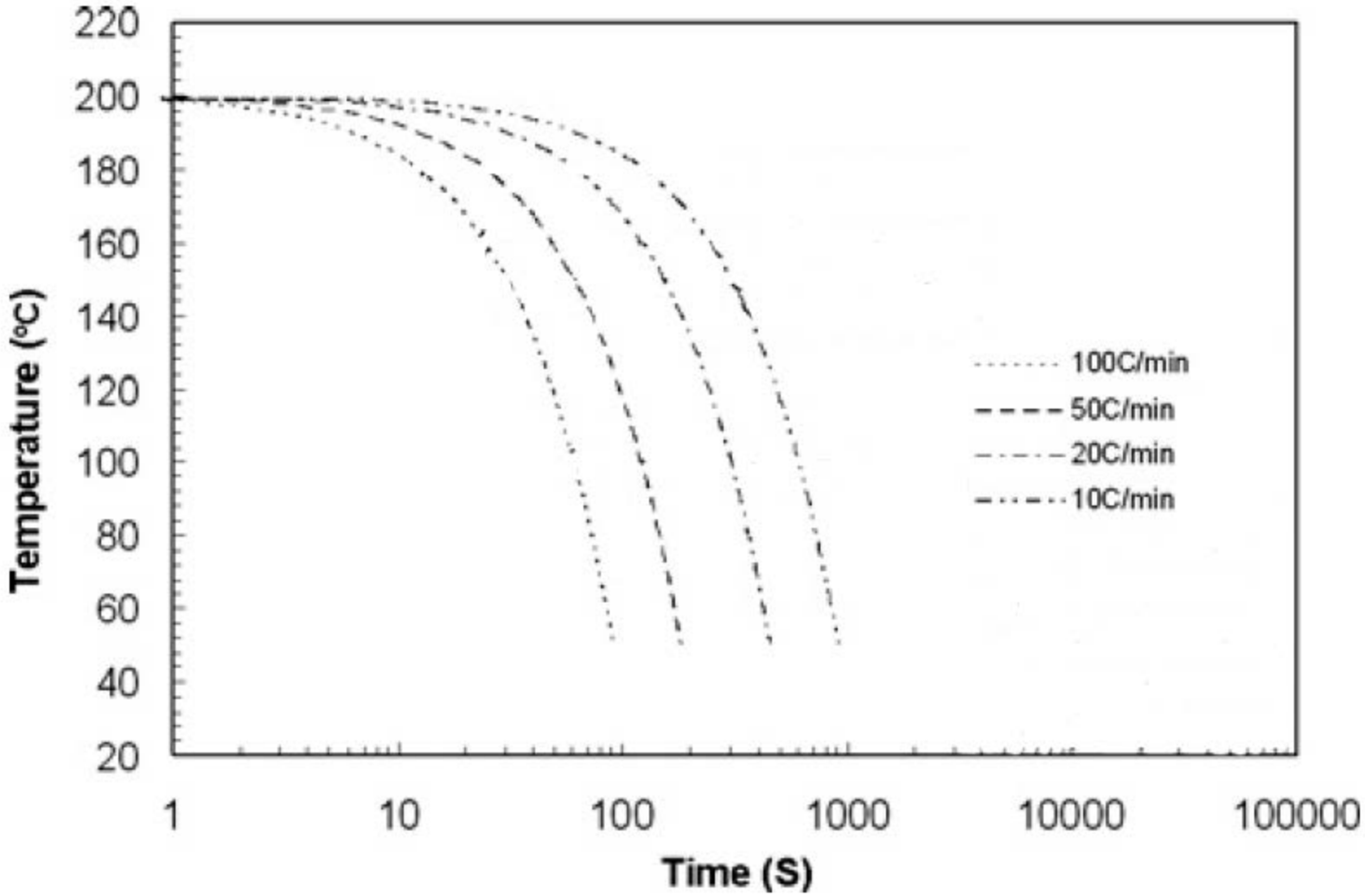
Measuring the Effect of Cooling Rate on the Transformation

The reorganization of the atoms to a new crystal structure takes some time.

If the material is cooled quickly there might not enough time for the transformation to occur before atomic mobility is too low for it to occur

Retention of hexagonal Cu_6Sn_5 as a metastable phase

Cooling Rates Studied



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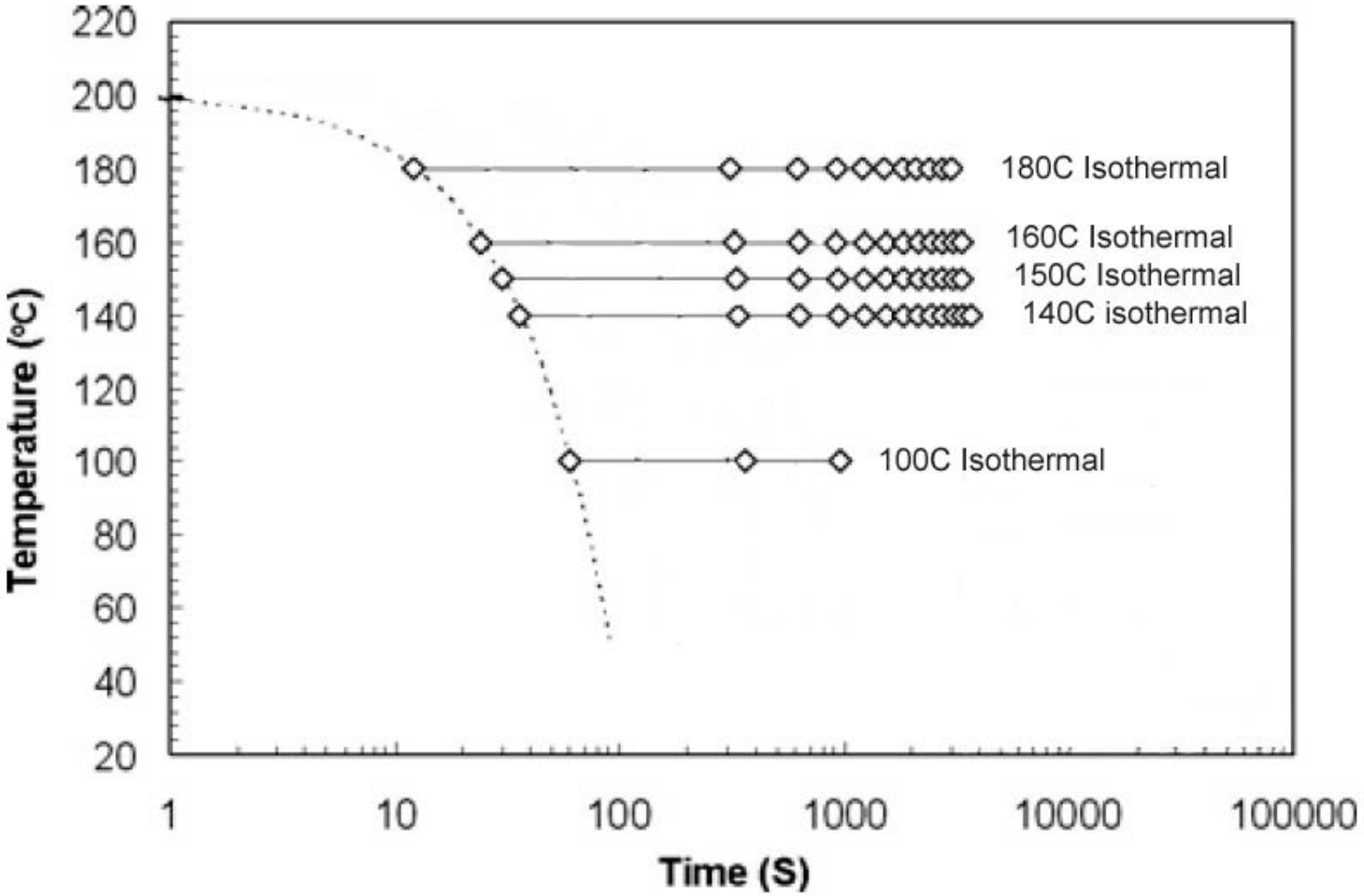
Isothermal Ageing of Rapidly Cooled IMC

- Stop the cooling and hold at a specific temperature for increasing times before quenching to room temperature to prevent further reaction.
- Monitor the progress of the transformation using X-Ray Diffraction for phase identification.

Isothermal Ageing of Rapidly Cooled IMC



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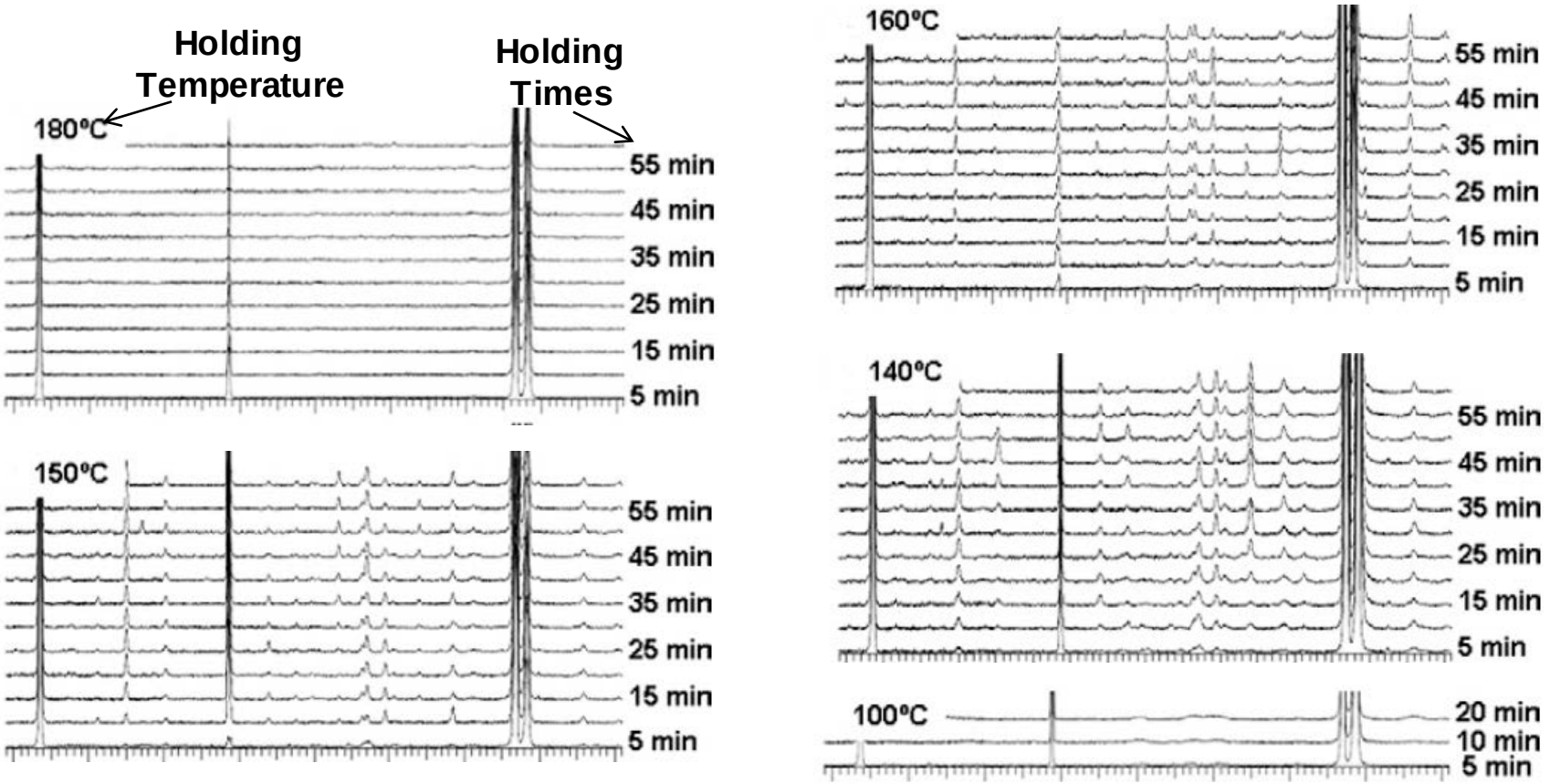
Isothermal Ageing of Rapidly Cooled IMC

Identifying Phases Present as a Function of Temperature and Time (Synchrotron XRD)



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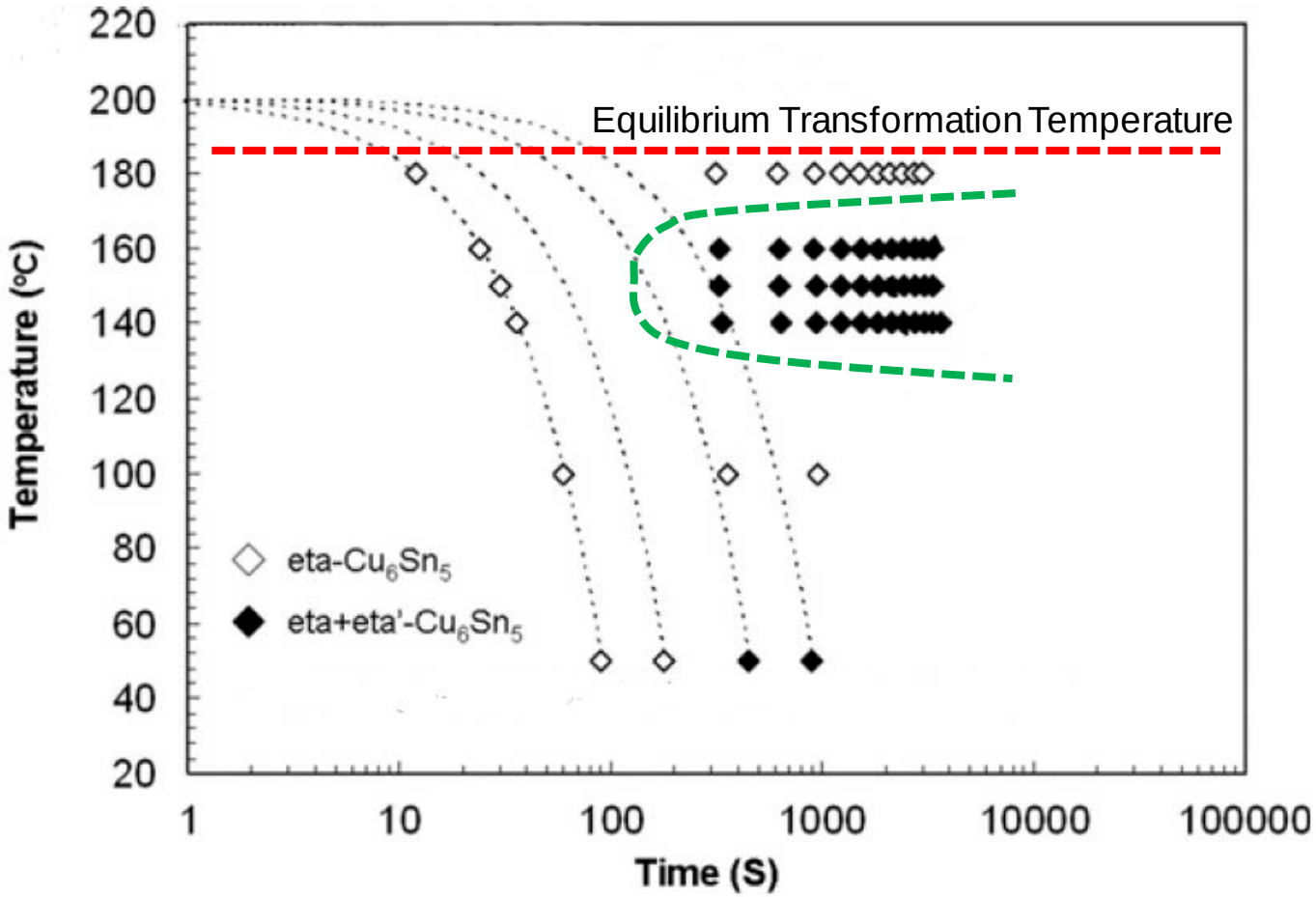

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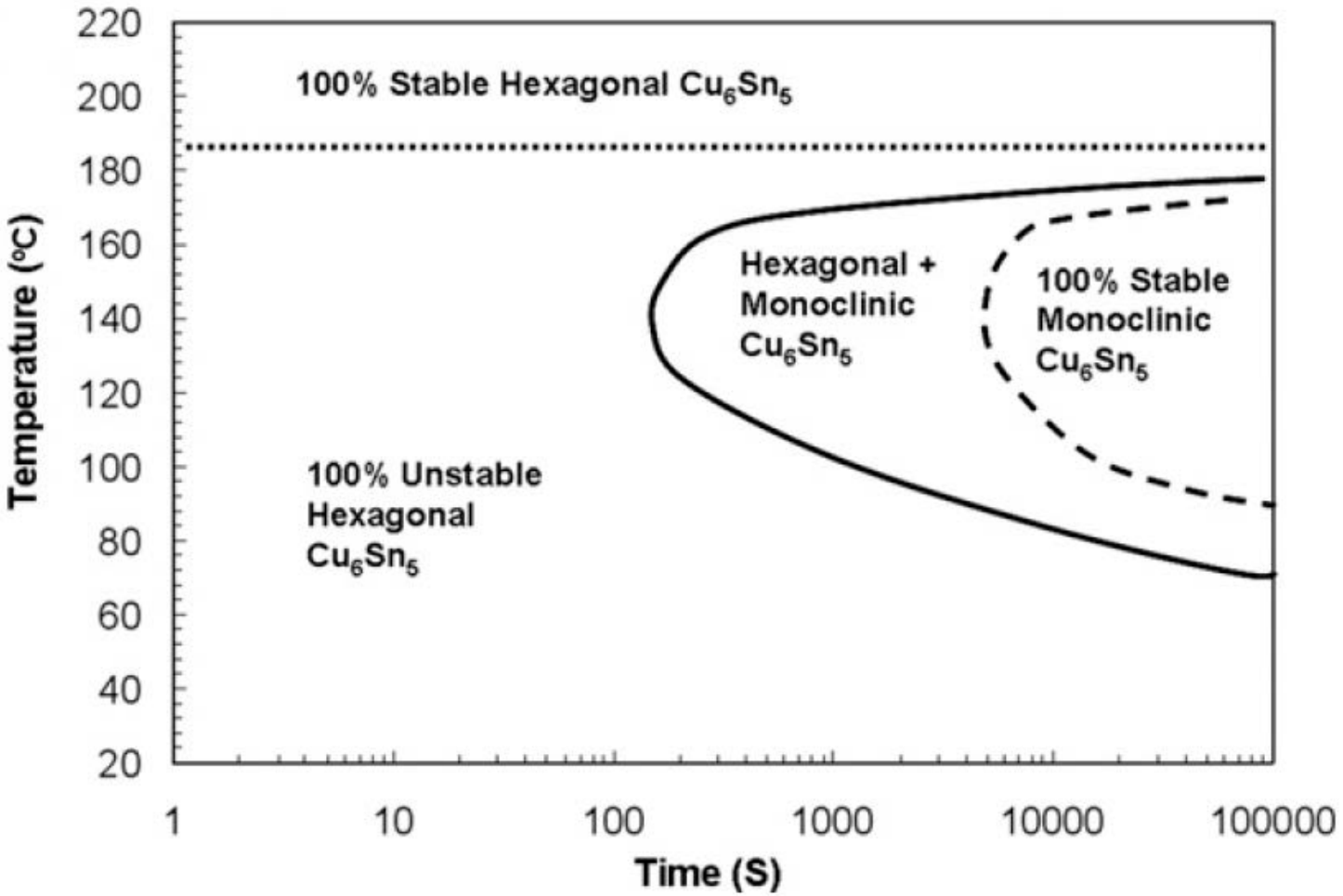
Proposed Temperature-Time-Transformation Diagram for Cu_6Sn_5



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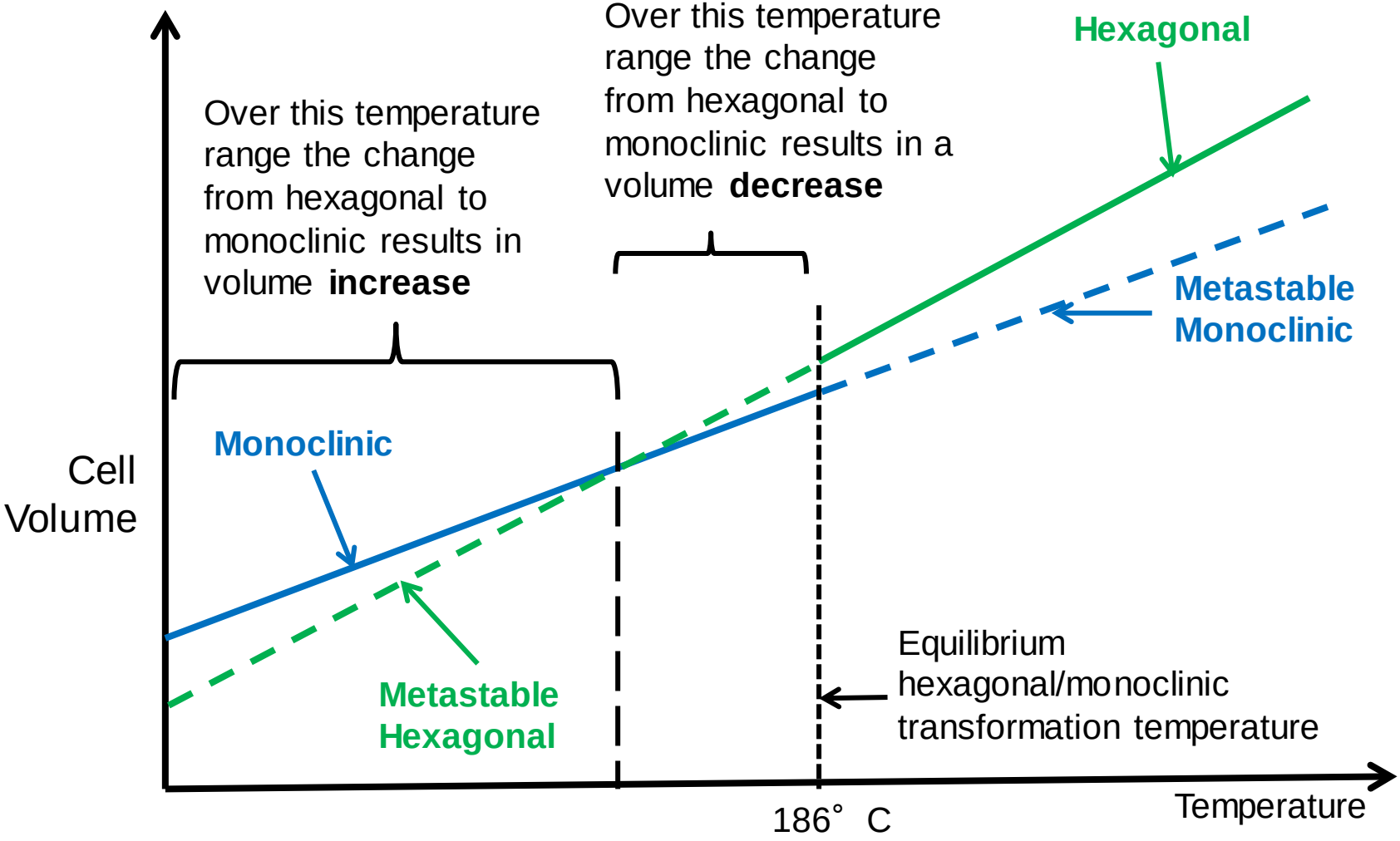
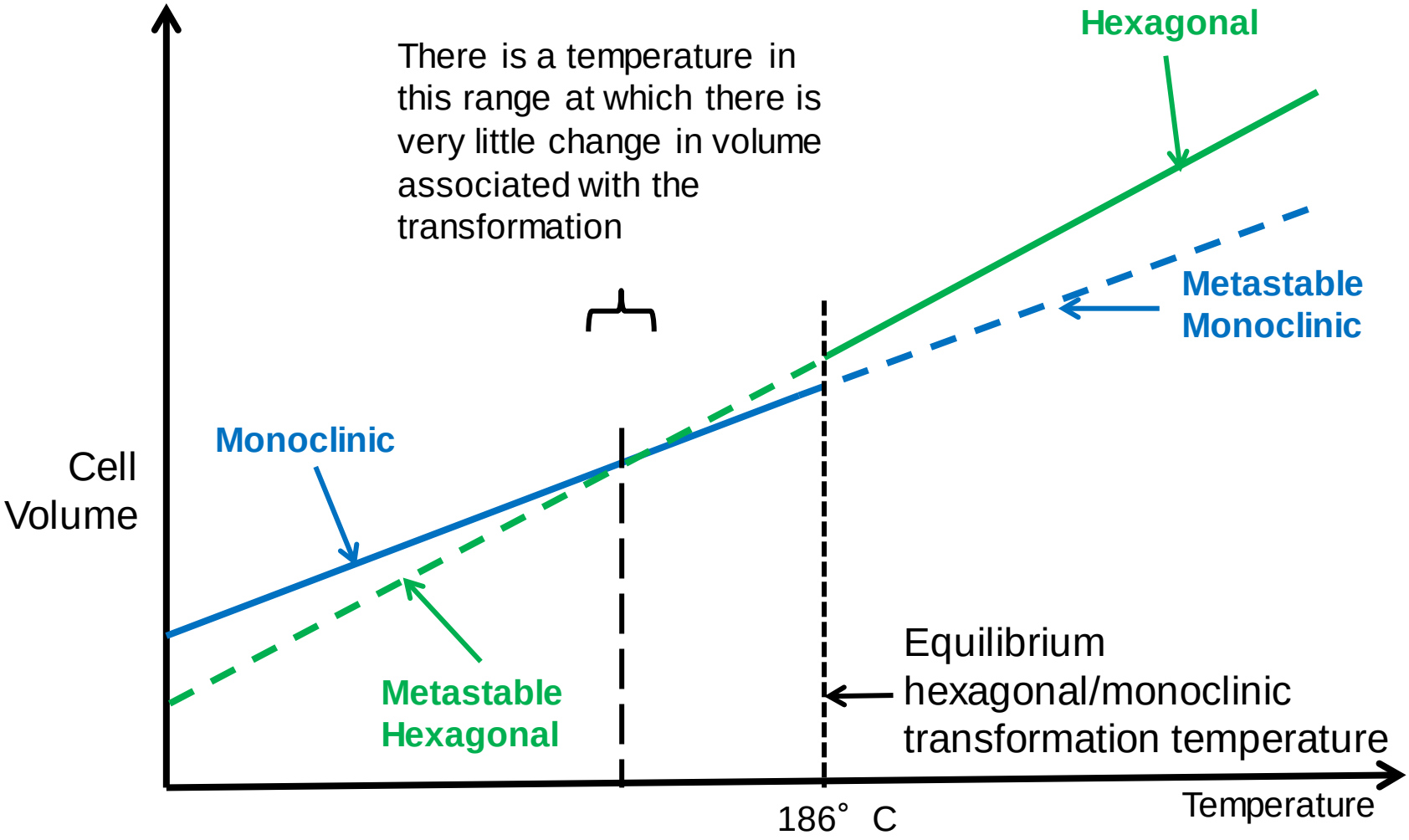
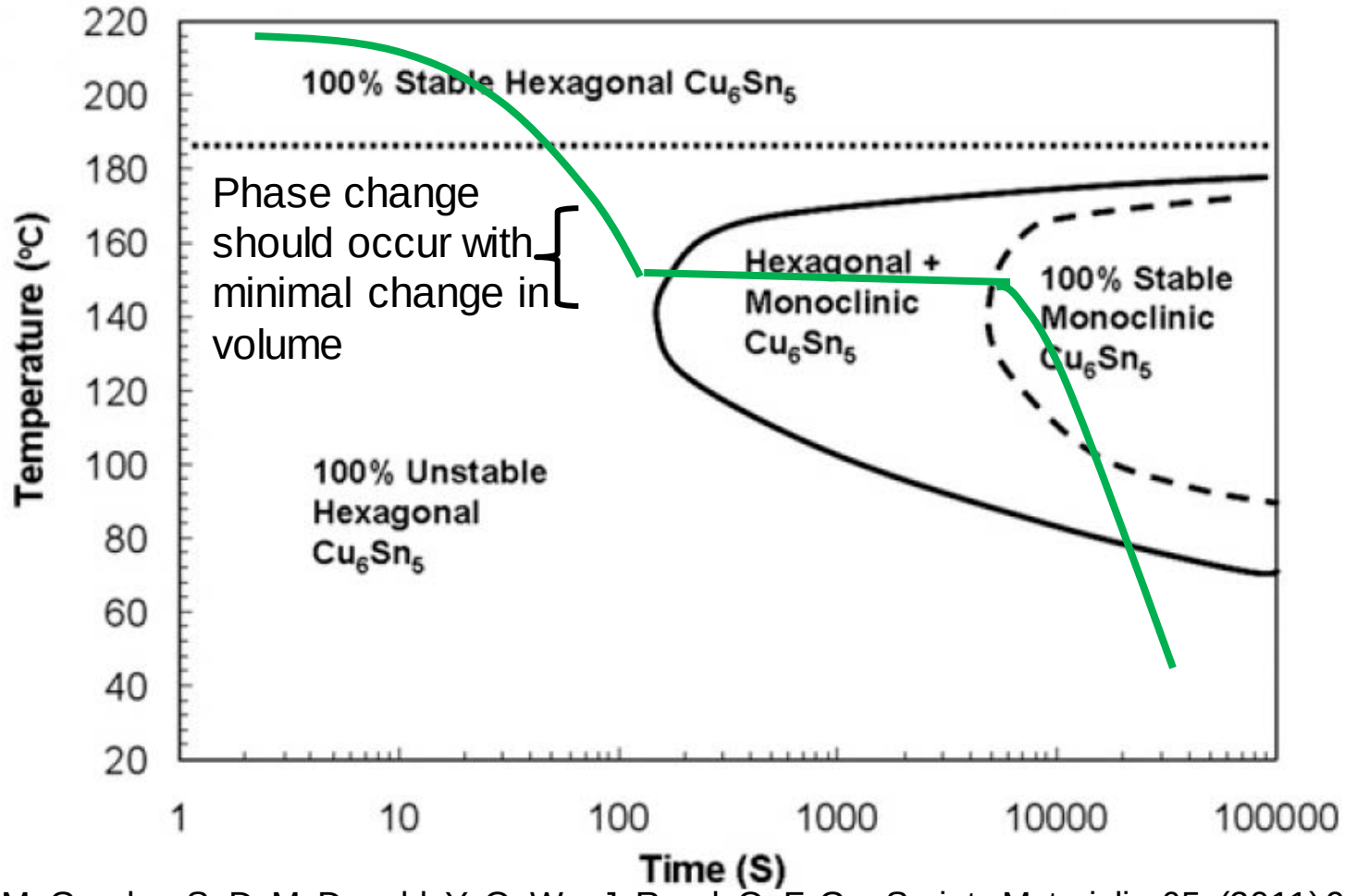
Volume change on η ↔ η' transition in Cu_6Sn_5?



Volume change on η ↔ η' transition in Cu_6Sn_5?



Post-solder Cooling Regime for Minimizing Damage Potential



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Conclusion

When the hexagonal form of the Cu_6Sn_5 has not been stabilized with an addition of Ni it could still be possible to minimize the potential detrimental effects of the hexagonal → monoclinic phase change by allowing the transformation to occur at a temperature at which the associated volume change is at a minimum.

This temperature appears to be around 150° C

Future Work

Continuing intensive study of the phase transformations and properties of stabilized and unstabilized Cu_6Sn_5.

Thank You