

Predicting Microstructure of Mixed Solder Alloy Systems

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ABSTRACT:

In the transition to lead-free soldering the potential for creating joints soldered with alloys of mixed and unknown composition will increase (e.g. through rework, repair, component finishes), raising questions on joint reliability. In this work the ability of a modelling tool, MTDATA, to predict the phases in the solder joints in such circumstances has been studied as a possible method in aiding rapid reliability assessment. Three experimental techniques (microsectioning, EDX analysis and DSC measurements) have been used to characterise the microstructure formed within the joints fabricated from various mixtures of SnPb and SnAgCu alloys. The results were compared directly with those on phase composition, enthalpy and heat capacity predicted from the MTDATA modelling. The encouraging agreement between the experimental data and the modelled predictions, demonstrates that the MTDATA tool may have a potentially key role in predicting alloy performance, especially in the transitional period towards lead-free soldering, and should be further investigated. The whole approach can yield benefits in studying the effect of alloy mixtures that arise from rework, a real possibility with advent of numerous lead-free alloys.

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ISSN 1473 2734

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Approved on behalf of Managing Director, NPL, by Dr C Lea,
Head, Materials Centre

CONTENTS

1	INTRODUCTION.....	2
2	EXPERIMENTAL.....	3
2.1	ASSEMBLY AND MATERIALS.....	3
2.2	MTDATA.....	3
3	RESULTS.....	4
4	DISCUSSION.....	6
4.1	COMPOSITION.....	7
4.2	COOLING.....	7
4.3	ENTHALPY AND HEAT CAPACITY.....	8
5	CONCLUSIONS.....	9
6	REFERENCES.....	10
7	ACKNOWLEDGEMENTS.....	10
8	APPENDIX A: MTDATA PLOTS.....	11
9	APPENDIX B: EDX RESULTS.....	19
10	APPENDIX C: DSC AND ENTHALPY RESULTS.....	23

1 INTRODUCTION

The industry is in a transitional stage in moving from soldering based on a tin-lead eutectic alloy to solders that are lead-free. This change is driven by the Waste Electrical and Electronic Equipment (WEEE) Directive from the European Union and global commercial pressures, with Japan in a pre-eminent position. However, not only has the industry not yet agreed on a single solder alloy replacement for the tin-lead solder (at least for mass soldering), but for reasons of cost, melting temperature, composition and compatibility, it is likely that a range of alloys may be used on a “horses courses” basis. Under such circumstances, and especially following rework, there will be great potential to create joints soldered with alloys of unknown composition. Work at the NPL in rework conditions and their effect on solder alloy composition has shown that complex quaternary alloys are formed in the liquidus^[1].

Currently, the leading lead-free alloy replacement is based around the SnAgCu eutectic alloy. This alloy has some very good characteristics, but it differs significantly from tin-lead with a melting point 34°C higher at 217 °C. If a solder joint manufactured from one alloy is repaired with the other alloy, then a quaternary alloy SnPbAgCu will be formed of undefined composition. If any of the other alternative lead-free alloys are used, then the scope for more alloy mixtures to be created increases rapidly.

Any new alloy would be microstructurally different to both SnPb and SnAgCu and may even contain new phases or intermetallics that would alter the joint characteristics of the solder. Intermetallics formed in these alloys were studied in previous work^[2]. Important issues that arise in creating new alloy mixtures are:

- Forming of intermetallics phases that may lead to re-crystallisation within a solder joint over a period of time, varying the strength characteristics. (e.g. during thermal cycling).
- Altering the ductile-brittle nature of the material.
- Varying the thermal coefficient of expansion of the alloy and hence change the performance from the expected design performance.
- Changing the surface tension will have an effect on solderability
- Increasing the of solder alloy pasty range

Irrespective of the precise alloy composition only certain microstructural phases will be formed on alloy solidification. The relative composition and the form of each phase will determine the mechanical performance of the alloy. The issue of concern is the alloy performance, and this is usually an expensive evaluation. A question to be answered is whether this evaluation need be carried out for all possible compositions. The work carried out at NPL highlighted the behaviour differences between 5 alloys reworked with 4 mixture ratios. However, what is the approach with new, previously uncharacterised, alloy compositions if long term reliability testing is to be avoided? Microstructural investigation offers useful information, and the occurrence and relative volume of phases are valuable pieces of information in predicting the performance of two similar alloys. If the microstructures of the two alloys are similar, and reliability evaluations have been carried out at compositional points over the range of interest, then a reasonable estimate of performance can be made.

Microstructural analysis can be a useful tool, but it does assume that a suitable specimen is available, and it will be time-consuming if a wide range of compositions are to be checked. Prediction of microstructure is possible based on thermodynamic data. Such a tool^[3], known as MTDATA, has been evaluated here. The MTDATA tool is used to predict the phases present in joints formed from mixtures of two solder alloys, and the results compared with those from a microstructural investigation on joints of the same alloy.

2 EXPERIMENTAL

2.1 ASSEMBLY AND MATERIALS

The substrate material used in the study was FR4 epoxy laminate with bare copper and OSP (organic solderability preservative). The components used were through-hole resistors (as shown in Figure 1) with solder combinations of SnPb and SnAgCu mixed in mass percentages of 25 and 75%. The SnPb composition was 68%Sn and 32%Pb and SnAgCu composition of 95.5%Sn, 3.8%Ag and 0.7%Cu. For manufacturing the alloys were mixed in solder paste form, and soldered using intrusive reflow techniques. The mass concentrations for each alloy mixture are:

- **Alloy A:** 25%SnPb and 75%SnAgCu: giving a total composition of Sn (87.1%), Pb (9.5%), Ag (2.1%) and Cu (0.5%).
- **Alloy B:** 75% SnPb and 25% SnAgCu: giving a total composition of Sn (70.4%), Pb (28.4%), Ag (1%) and Cu (0.2%).

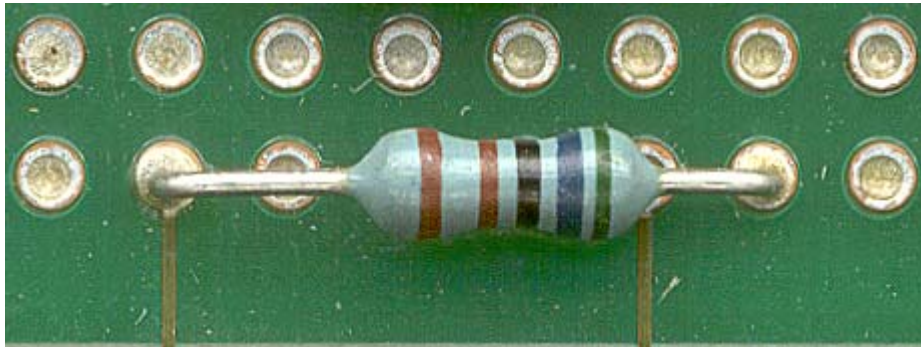


Figure 1. Example of a through-hole resistor.

2.2 MTDATA

MTDATA is a software package for the calculation of phase equilibria in multicomponent multiphase systems using, as a basis, critically assessed thermodynamic data. It has numerous applications in the fields of metallurgy, chemistry, materials science, and geochemistry depending only on the data available. Problems of mixed character can be handled, for example equilibria involving the interaction between liquid and solid alloys and matte, slag and gas phases. The thermodynamic models necessary to describe the properties of a wide range of

phase types are incorporated in the software and database structures. It can be used in various ways to predict the formation of solutions, compounds, intermetallics and phases through phase diagrams and thermo-chemical calculations.

In this work, MTDATA was used to predict phases and their mass fraction for the alloy combinations. In the model two cooling rates were used, “Scheil” (representing a fast cool or a quench) and “equilibrium” (slow cool).

Energy-dispersive X-ray analysis (EDX) and Differential Scanning Calorimetry (DSC) were used to characterise the solders formed in the two alloys, and the results were compared with the MTDATA predictions.

3 RESULTS

Micrographs of microsections of typical joints of through-hole resistors formed using two solder mixtures are shown in Figures 2 and 3. The phases detected were designated as A to D, and listed in Table 1.

The results of MTDATA calculations are presented in Figures 4 to 15 in Appendix A. These results include calculations for the relative masses of phases present, enthalpy changes and changes in the heat capacity for both Scheil and equilibrium cooling condition.

The phases marked A to D in Figures 2 and 3 were analysed for composition using the spot mode of the EDX technique, and the resulting spectra are presented in Appendix B, Figures 16-23. The phases found are summarised in Table 1. Since many of the precipitates were irregular in shape and micrometre in size, it was not possible to acquire unique spot analyses from all the individual phases, since the EDX signals would contain contributions from the surrounding material. However, the analyses of the copper-tin phases provided a strong indication that the intermetallic was Cu_6Sn_5 and not Cu_3Sn . Similarly, analyses of the silver-tin phases confirmed the intermetallic as Ag_3Sn . It was not possible to determine the volume fraction of each phase from these studies, which would have required a sophisticated area measurement tool.

The DSC measurements were made using the modulated mode, and the results for specific heat are presented in Appendix C (Figures 24 and 25), for which the solder mixtures were heated to 550K. The integral of these curves, the enthalpy of fusion, is also included in these Figures.

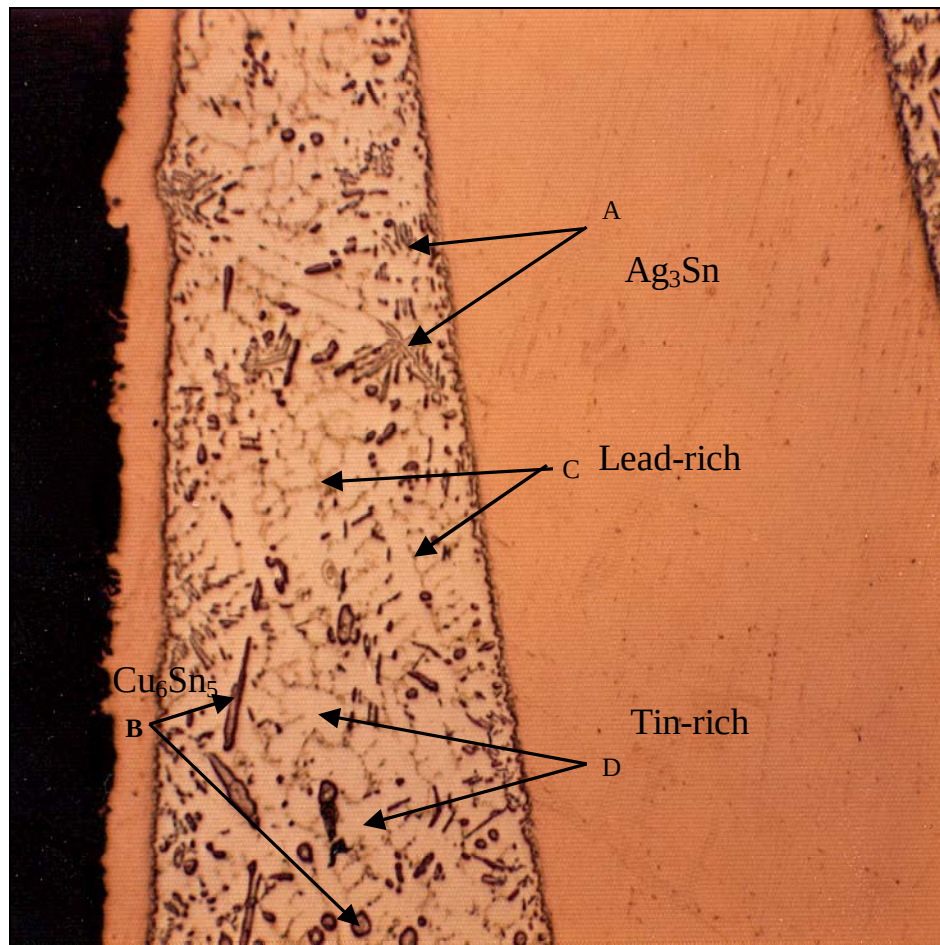


Figure 2. Alloy A, SnAgCu/ 25% SnPb, TH-Resistor joint (x390).

Table 1: Result of EDX Analysis

Alloy Mixture	Microsection reference letter	Main Constituent	Secondary Constituent	Phase
A	A	Silver	Tin	Ag_3Sn
	B	Tin	Copper	Cu_6Sn_5
	C	Lead	-	Lead-rich phase
	D	Tin	-	Tin-rich phase
B	A	Silver	Tin	Ag_3Sn
	B	Tin	Copper	Cu_6Sn_5
	C	Lead	-	Lead-rich phase
	D	Tin	-	Tin-rich phase

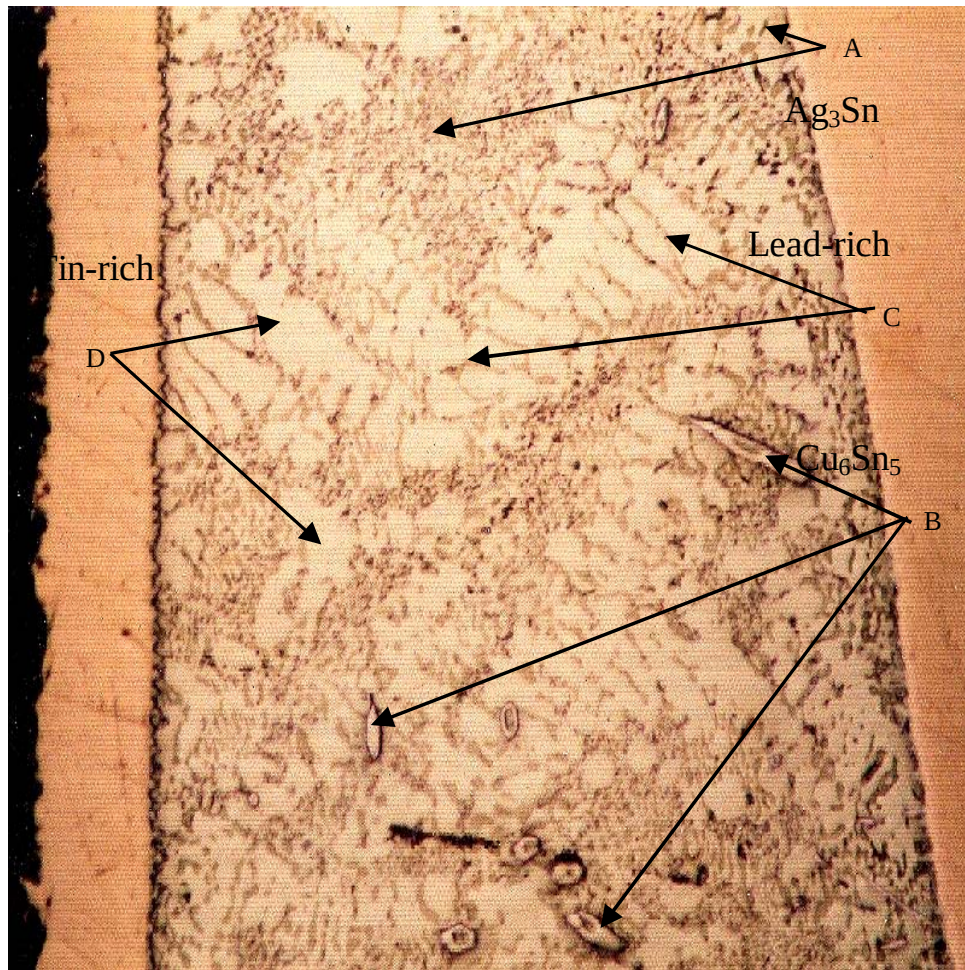


Figure 3. Alloy B, SnAgCu/ 75% SnPb, TH-Resistor joint (x440).

4 DISCUSSION

The key question in this study was whether the model accurately predicts the phase composition and the thermo-dynamic properties of actual solder joints formed using mixed alloy systems. It is convenient, therefore, to compare in turn the various sets of predicted data from the MTDATA modelling with those obtained experimentally.

4.1 COMPOSITION

MTDATA predictions of the phases present and of their composition indicate (Figures 4-7) the presence of four main phases (Ag_3Sn ; Cu_6Sn_5 ; a FCC Pb-rich phase; a BCT Sn-rich phase; plus a few minor phases at <1%), and this is in good agreement with the EDX results (see Table 1).

The MTDATA modelling also provides additional information on the volume fraction forming with temperature, and the overall liquid fraction. This is particularly useful in that it indicates the range over which the liquid freezes and the rate at which the composition changes. For alloy mix A the solidification initiates at 478K, and becomes fully solid at 451K, where the last 25% freezes at this lower temperature. However, for alloy mix B solidification initiates at 463K and finishes at 453K where the last 75% freezes at the lower temperature. The contrast in the heat capacity plots shows clearly the increasing SnPb in alloy B is influential in altering the overall behaviour.

Unfortunately, the EDX technique cannot provide information on the amounts of phases formed, and hence it was not possible to verify the modelling prediction regarding volume fractions formed.

4.2 COOLING

Under actual assembly conditions, a board experiences only a single cooling rate, as it passes from the high temperature soldering zone into a forced air-cooled zone (cooling rate typically 10C sec⁻¹). However, for the modelling exercises it was possible to consider two cooling rates:

- virtually instantaneous, as in a quench, and known as Scheil
- equilibrium cooling, which is very slow

Figures 4-7 highlight which phases form first. In the case of alloy mix A these are Cu_6Sn_5 and then Ag_3Sn and the BCT Sn-rich phase, followed by the FCC Pb-rich phase. In the case of alloy B the order of formation is Cu_6Sn_5 , then the BCT Sn-rich phase followed by the Ag_3Sn and FCC Pb-rich phases. It is interesting to note that whilst the BCT phase forms over a wide temperature range, the Pb-rich FCC phase forms quickly over a narrow temperature range. This difference between the rates of formation of BCT and FCC phases, underlines a number of differences observed between alloy mixes A and B reflecting their relative compositions. The cooling rate will affect both grain size and microstructure. Although the model doesn't provide grain size, it does give some microstructure information. The modelling data for the two cooling regimes suggest very little difference in the amounts of the BCT and FCC phases present, but the Scheil cooling does produce higher levels of the Cu_5Sn_6 and then Ag_3Sn intermetallics forming. The increased formation, or precipitation, of these intermetallics is consistent with quenching in many allot systems.

The predicted solidification range from the model is useful in revealing the likely pasty range of the alloy (temperature range between solid and liquid states), which has been shown to be important in defining the susceptibility of an alloy to the fillet lifting phenomenon.

4.3 ENTHALPY AND HEAT CAPACITY

The results of the MTDATA modelling of the enthalpy changes during solidification for alloys A and B are shown in Figures 8 to 11. For each alloy there is little difference in the data for the two cooling rates. The data for both alloys exhibit a small temperature region around 450K where the gradient is lower for the equilibrium cool. The enthalpy curves for alloy mix A show a gradual decrease in energy between 480 and 455K, in agreement with the liquid fraction observed in Figures 4 and 5. At 455K the gradient becomes much steeper as the FCC phase forms quickly. With alloy mix B and the higher content of the FCC phase this part of the curve is more extensive with concomitant greater energy loss. The presence of the intermetallics Cu₅Sn₆ and Ag₃Sn have no perceptible impact on the enthalpy curves, probably due to their low concentrations.

The heat capacity curves are presented in Figures 12 –15 for the two alloy mixes. Small differences, similar to those in the enthalpy curves, are again present, but now at 448K. The heat capacity curves are simply the differential of the enthalpy curves, but perhaps show more clearly the latent heat of freezing than the enthalpy curves. The heat capacity curves also show that most of the energy is lost at a single temperature for alloy mix B, whereas for alloy mix A it is spread over a range between two peaks.

The experimental DSC results for heat capacity are presented in Figures 24 and 25 and can be compared directly with the predicted curves (see Figures 12-15). Encouragingly, the comparison shows that the two sets of curves are similar with the agreement being better for alloy mix A than for alloy mix B. The peak positions for the predicted and measured specific heat agree very closely (see Table 2).

Table2: Specific heat and enthalpy data for Alloy A & B

	Alloy	Cp J.K⁻¹.mol⁻¹	Enthalpy J.mol⁻¹	Peak Position (K)
Measured	A (25SnPb,75SAC)	331, 346	74.9 x 10 ³	452, 475
	B (75SnPb,25SAC)	530, 180	25.3 x 10 ³	451, 461
MTDATA	A (25SnPb,75SAC)	900, 580	53.7 x 10 ³	451, 478
	B (75SnPb,25SAC)	2848, 189	90.5 x 10 ³	451, 460

A limitation of the DSC technique is its ability to react to sharp changes with temperature (e.g. the peak at 451K) which distorts the peak shape making it wider and shorter. A full discussion

of peak distortion caused by the thermal lag in the system is given in Reference 6. To overcome some of these difficulties it is sometimes beneficial to consider enthalpy, calculated by integrating the specific heat data, which is less sensitive to sharp changes with temperature. Such enthalpy data are also included in Figures 24 and 25, from which a comparison of the absolute changes in enthalpy over the temperature range 445 to ~480K can be made. The specific heat and enthalpy data for the two alloy mixes for both MTDATA modelling and DSC measurements, are given in Table 2. Although the enthalpy data for alloy mix A agree within 30%, the agreement for alloy mix B is much poorer, and this is attributed to the limitations of the experimental method used (e.g. thermal lag, and the sharp melting point of the eutectic SnPb).

5 CONCLUSIONS

This study has investigated the ability of a modelling tool, produced at the NPL called MTDATA, to predict phases in solder alloy mixtures containing SnPb and SnAgCu solder. Mass percentages of 75% SnPb, 25% SnAgCu and 25% SnPb, 75% SnAgCu solder mixtures were used to assemble through-hole solder joints. Three practical techniques were used to analyse and compare the phases present within the joints i.e. microsectioning, EDX analysis and DSC. The results obtained from these analytical methods were compared directly with the results obtained from the MTDATA modelling program. The investigation revealed the following:

- Microsectioning: The main phases and intermetallics present in the microsections of joints of both solder alloy combinations were consistent with MTDATA predictions.
- EDX Analysis: The elemental analysis confirmed the composition predicted by MTDATA.
- DSC: The specific heat measurements correlated approximately with the MTDATA values. Better agreement was achieved with the enthalpy values. The sharpness of the SnPb melting point is a measurement challenge to obtain accurate data.

The overall conclusion from this short study is that MTDATA can be effective in predicting the phases in solder joints formed using mixtures of two solders. Further work should be undertaken to explore the full potential of this particular modelling technique. With a more comprehensive materials database available within MTDATA, the modelling technique could be used for a wider range of solder systems. In consequence, the MTDATA tool has the potential for use as a predictive tool in the assessment of the reliability of joints formed with new, or mixed, solders. **Hence, the work has potential benefits in a rework scenario, where mixing lead-free alloys is unavoidable.** Once the intermetallic phases have been successfully predicted, their impact on joint reliability following thermo-mechanical fatigue can be estimated.

6 REFERENCES

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- [5] <http://www.npl.co.uk/npl/cmmt/cog/thermal.html#DSC>.
- [6] Differential Scanning Calorimetry: An Introduction for Practitioners. G. Höhne, W. Hemminger, H-J. Flammersheim. Published by Springer, ISBN 3-540-59012-9, Chapter5.4, Desmearing of the DSC curve

7 ACKNOWLEDGEMENTS

This work was carried out as part of a project in the Measurements for the Processability of Materials (MPM7.3) Programme of the UK Department of Trade and Industry. The authors are grateful to Hugh Davies for assistance in the understanding and use of the NPL produced modelling program, MTDATA.

8 APPENDIX A: MTDATA PLOTS

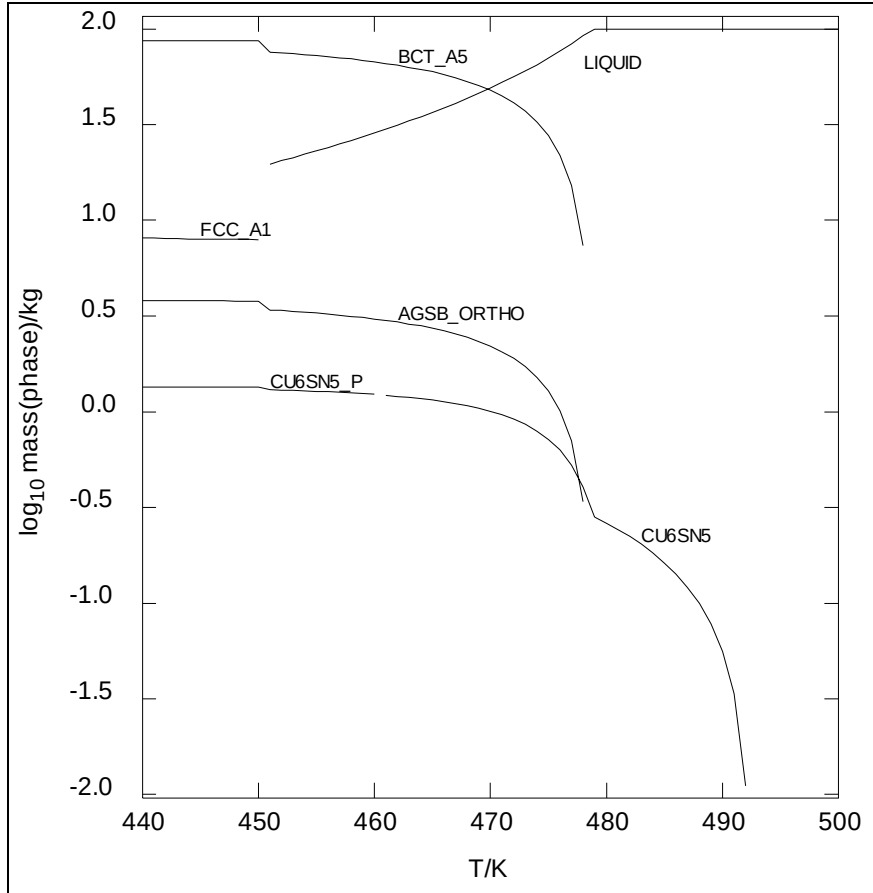


Figure 4. Phase formation plot for alloy A, equilibrium cooled.

The key for the labels in Figure 4, and hence the phases present are:

- BCT_A5: Body centred tetragonal Sn-rich phase
- FCC_A1: Face centred cubic Pb-rich phase
- AGSB_ORTHO: Ag₃Sn acicular phase
- CU6SN5_P: Cu₆Sn₅ globular phase

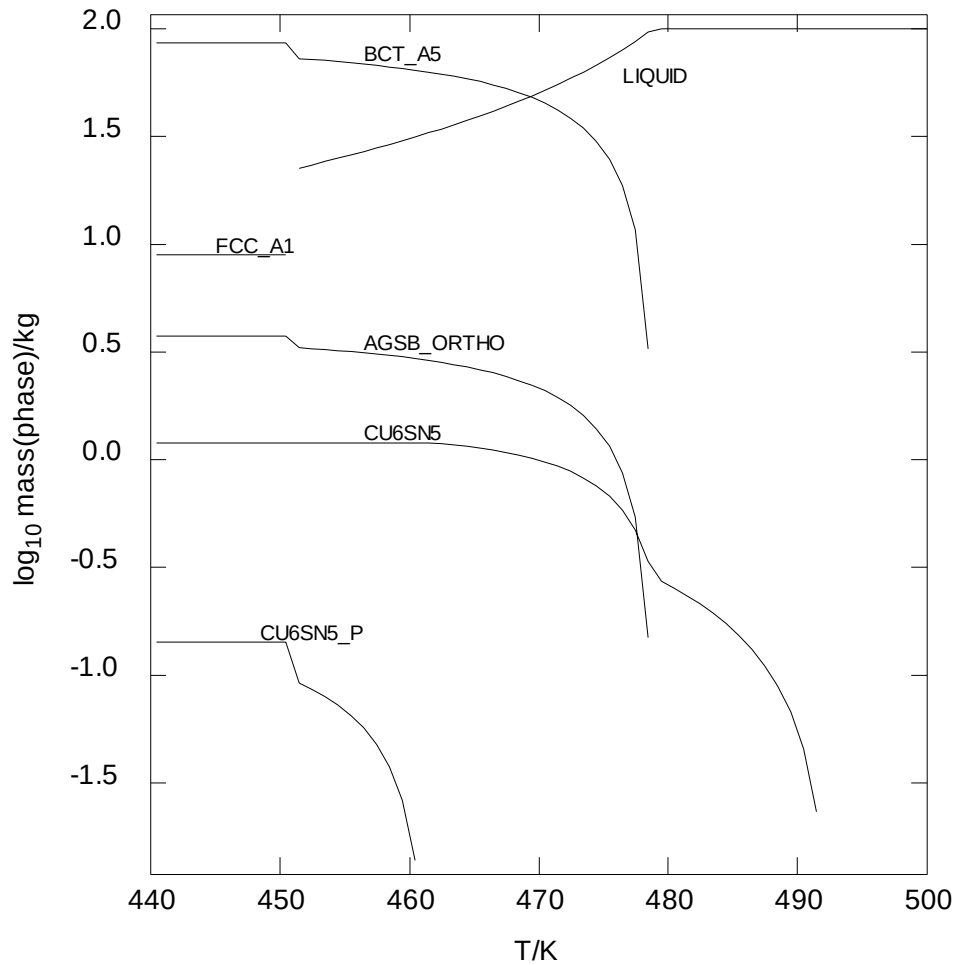


Figure 5. Phase formation plot for alloy A, Scheil cooled.

The key for the labels in Figure 5, and hence the phases present are:

- BCT_A5: Body centred tetragonal Sn-rich phase
- FCC_A1: Face centred cubic Pb-rich phase
- AGSB_ORTHO: Ag_3Sn acicular phase
- 10: CU6SN5_P: Cu_6Sn_5 globular phase
- 1: CU6SN5_P: Cu_6Sn_5 globular phase
- 13: CU6SN5_P: Cu_6Sn_5 globular phase

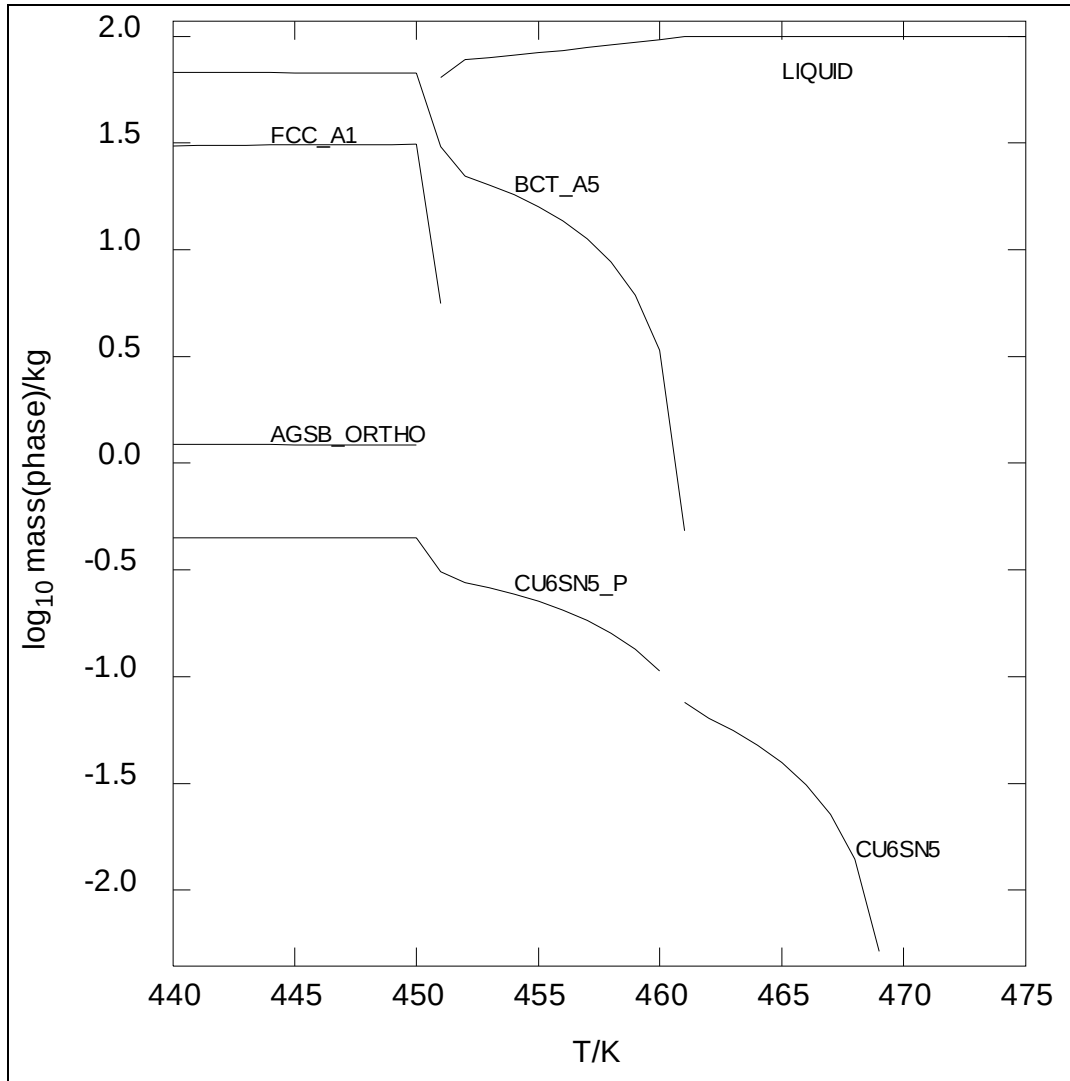


Figure 6. Phase formation plot for alloy B, equilibrium cooled.

The key for the labels in Figure 6, and hence the phases present are:

- BCT_A5: Body centred tetragonal Sn-rich phase
- FCC_A1: Face centred cubic Pb-rich phase
- AGBS_ORTHO: Ag_3Sn acicular phase
- CU6SN5_P: Cu_6Sn_5 globular phase

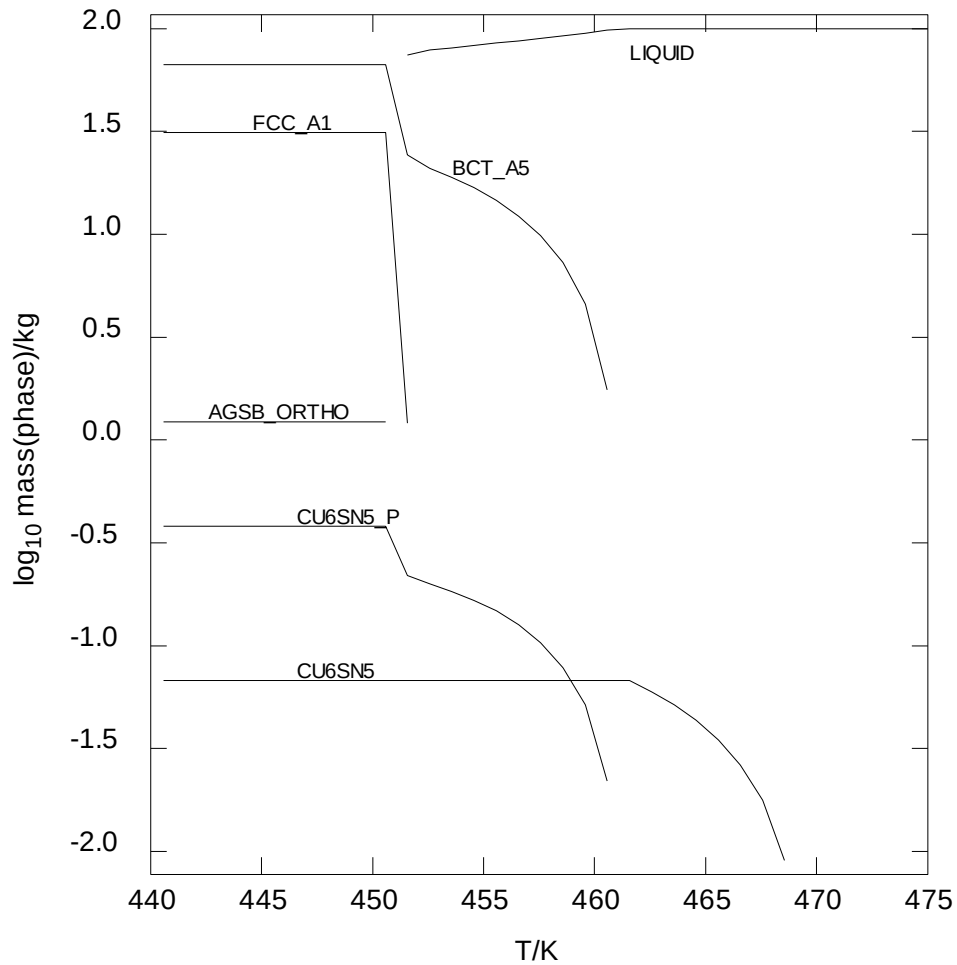


Figure 7. Phase formation plot for alloy B, Scheil cooled.

The key for the labels in Figure 7, and hence the phases present are:

- BCT_A5: Body centred tetragonal Sn-rich phase
- FCC_A1: Face centred cubic Pb-rich phase
- AGSB_ORTHO: Ag_3Sn acicular phase
- 14: Cu_6Sn_5 globular phase
- 12: Cu_6Sn_5 globular phase
- 1 Cu_6Sn_5 globular phase
- 10: Cu_6Sn_5 globular phase

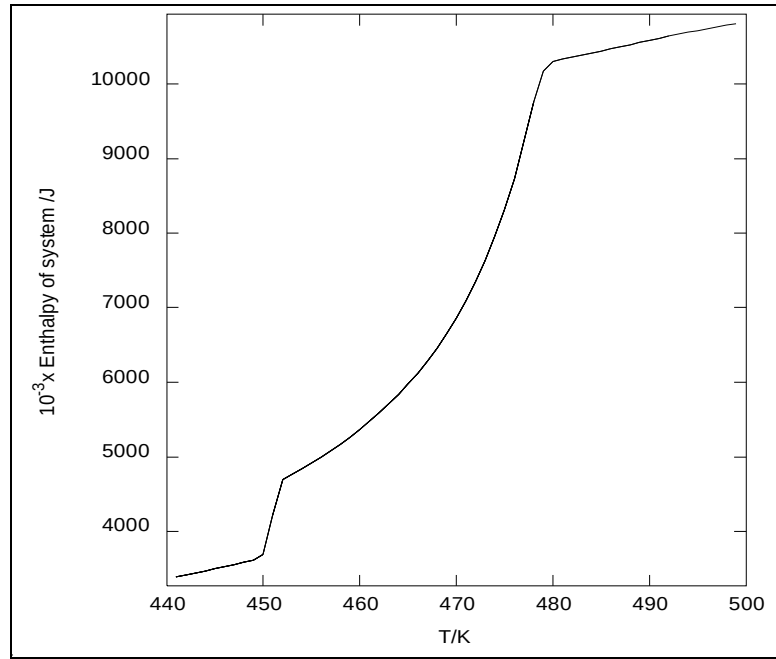


Figure 8. MTDATA plot of enthalpy for alloy A during equilibrium cooling.

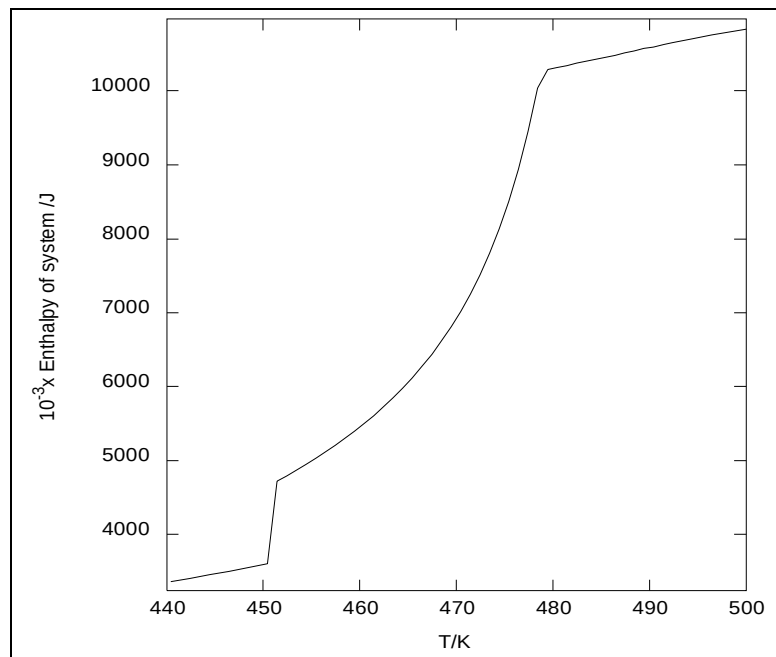


Figure 9. MTDATA plot of enthalpy for alloy A during Scheil cooling

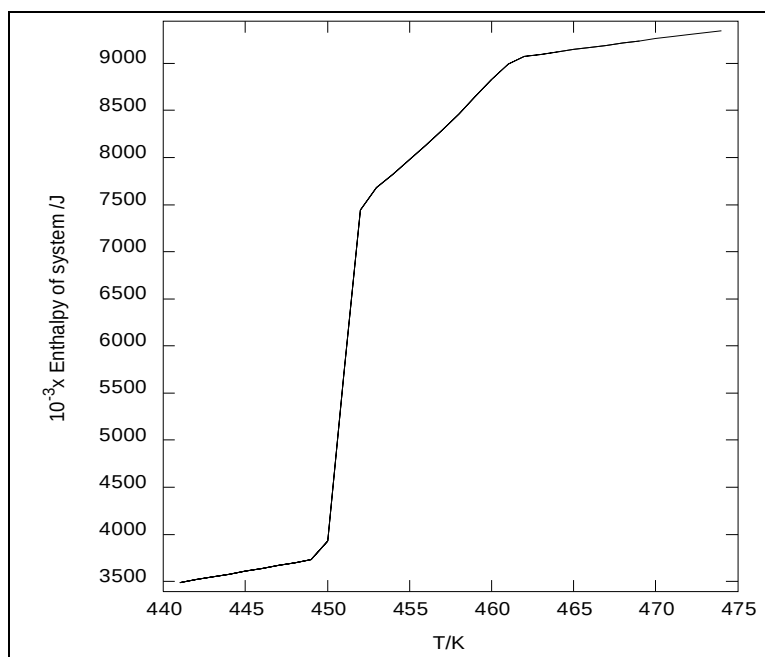


Figure 10. MTDATA plot of enthalpy for alloy B during equilibrium cooling.

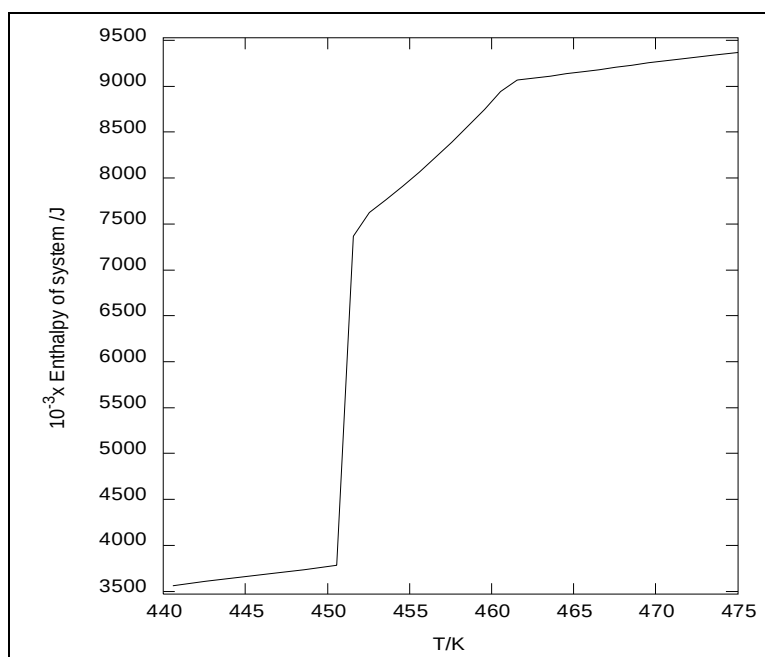


Figure 11. MTDATA plot of enthalpy for alloy B during Scheil cooling

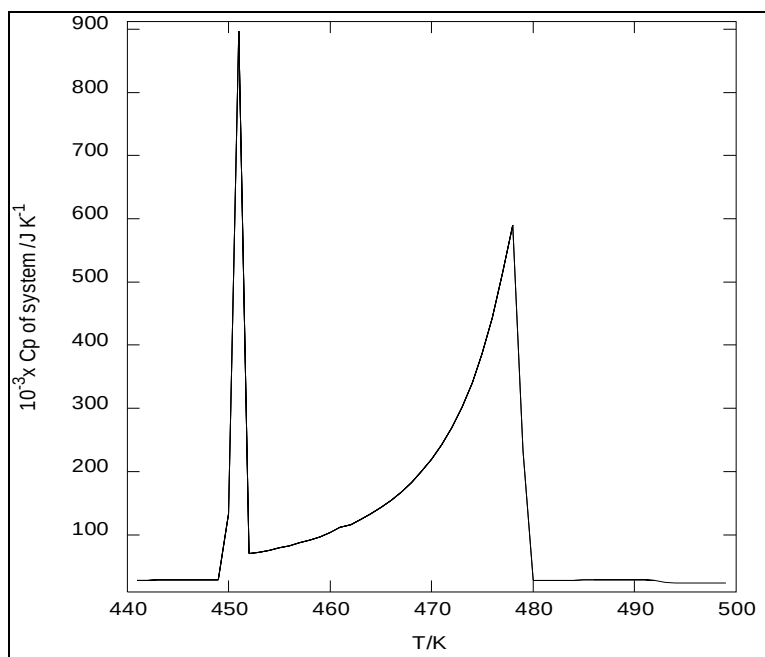


Figure 12. MTDATA plot for heat capacity change for alloy A during equilibrium cooling.

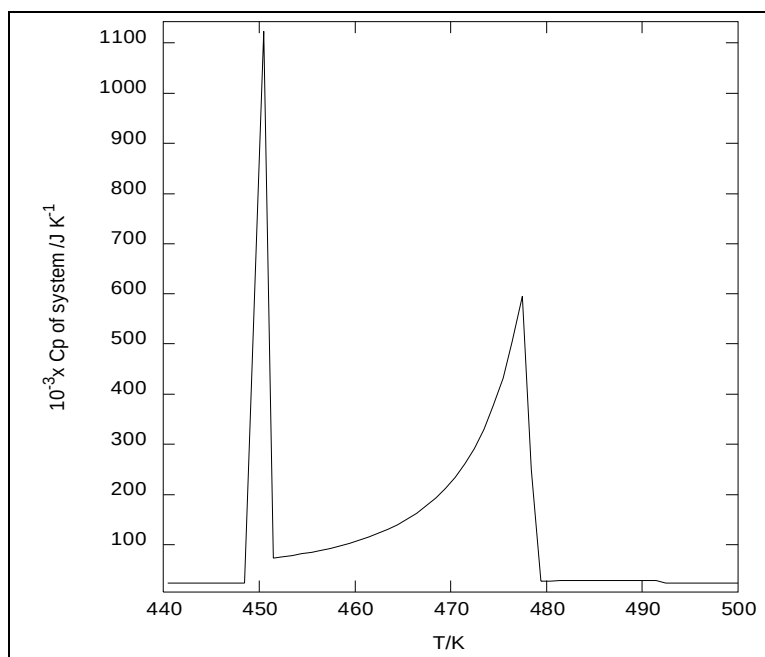


Figure 13. MTDATA plot for heat capacity change for alloy A during Scheil cooling.

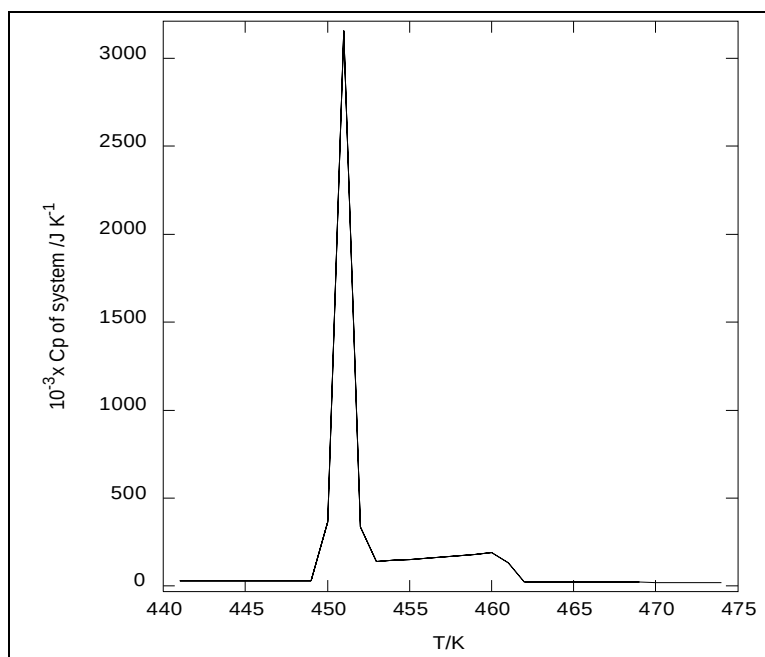


Figure 14. MTDATA plot for heat capacity change for alloy B during equilibrium cooling.

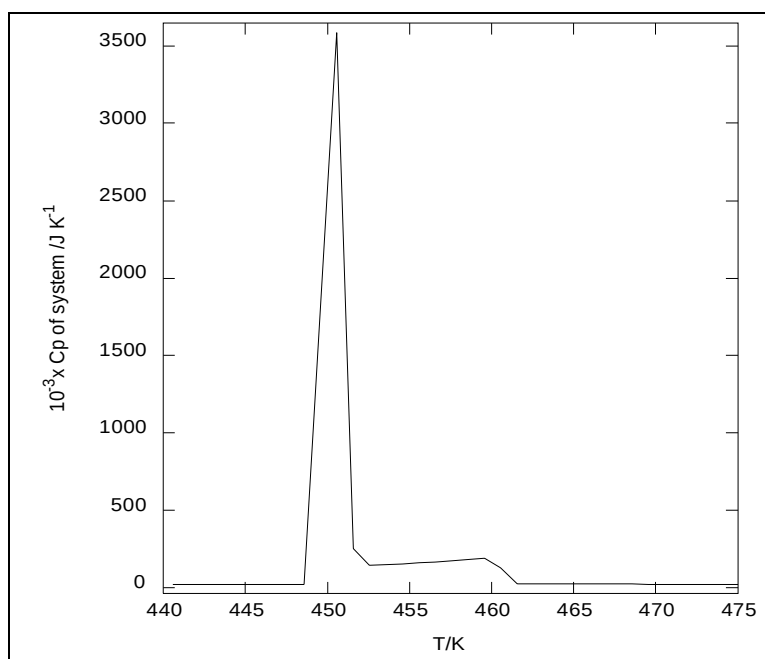


Figure 15. MTDATA plot for heat capacity change for alloy B during Scheil cooling.

9 APPENDIX B: EDX RESULTS

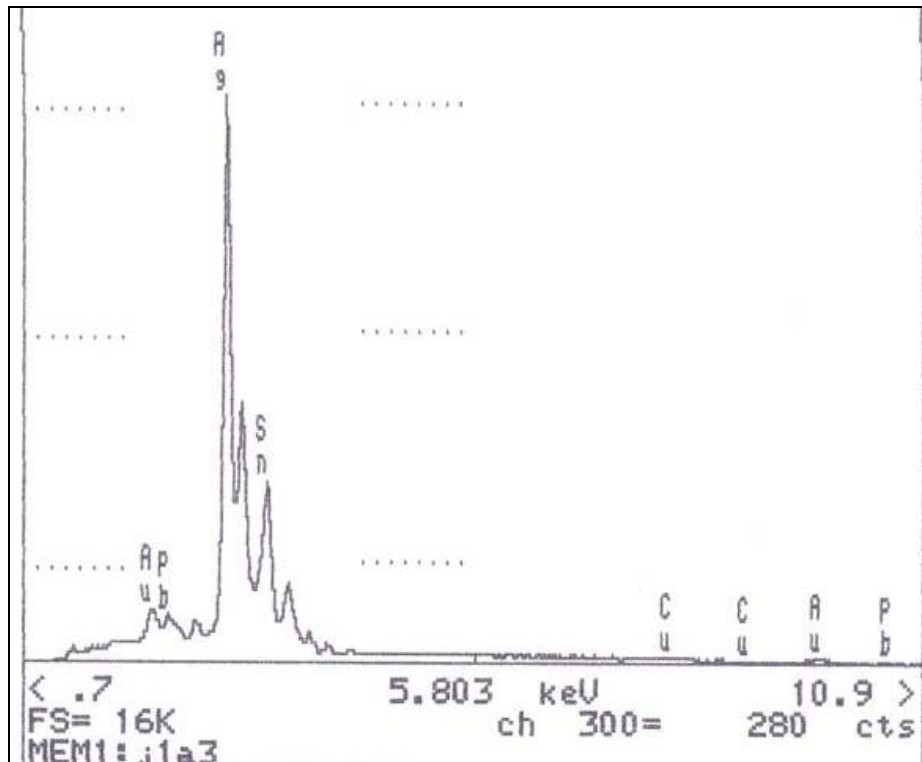


Figure 16: Position A in Figure 2, revealing silver-rich acicular phase

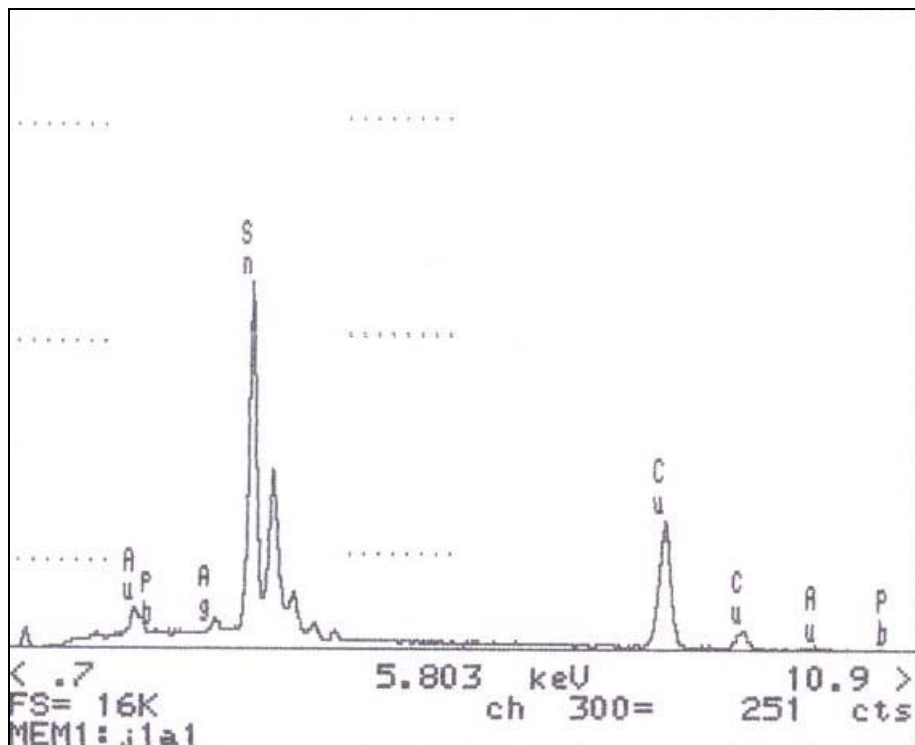


Figure 17: Position B in Figure 2, revealing SnCu intermetallic

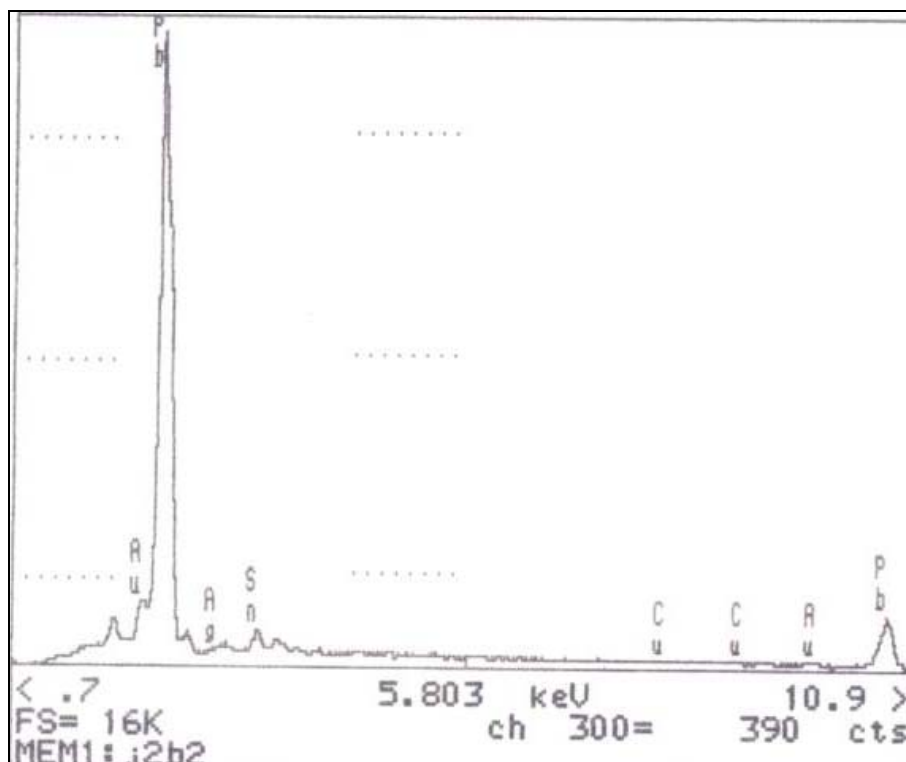


Figure 18: Position C in Figure 2, revealing lead-rich lamellae phase

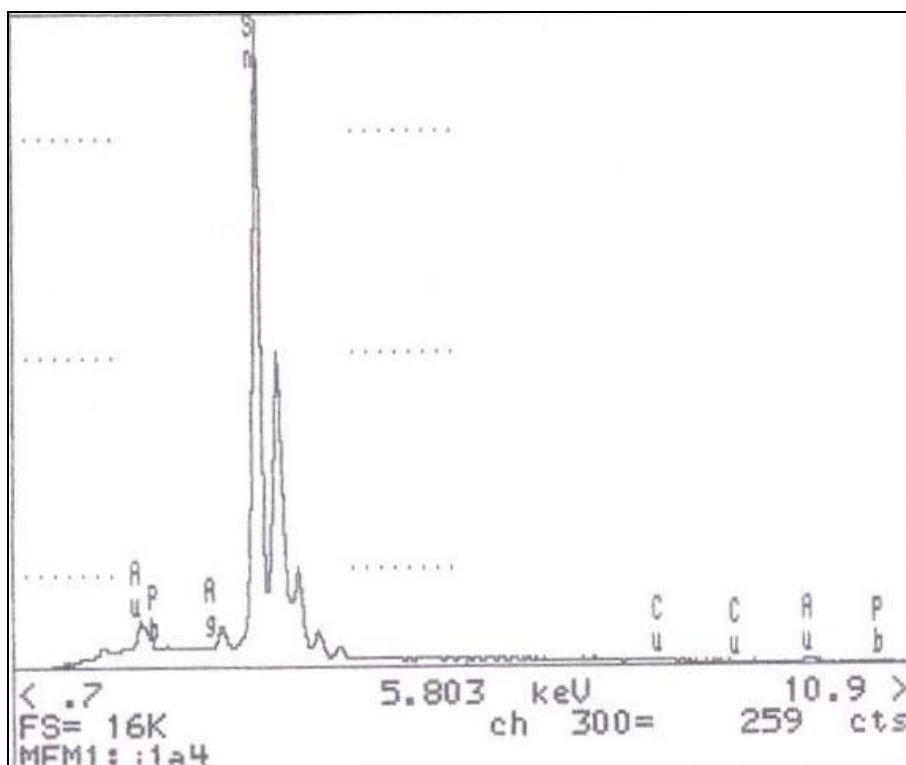


Figure 19. Position D in Figure 2, revealing Sn-rich globular phase.

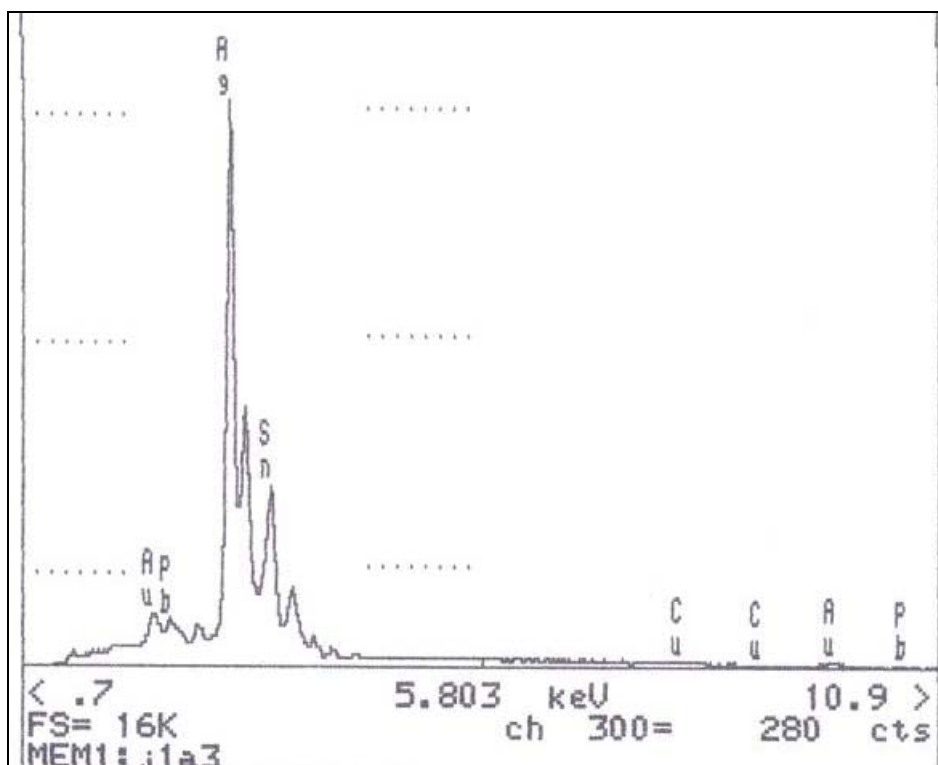


Figure 20: Position A in Figure 3, revealing silver-rich acicular phase.

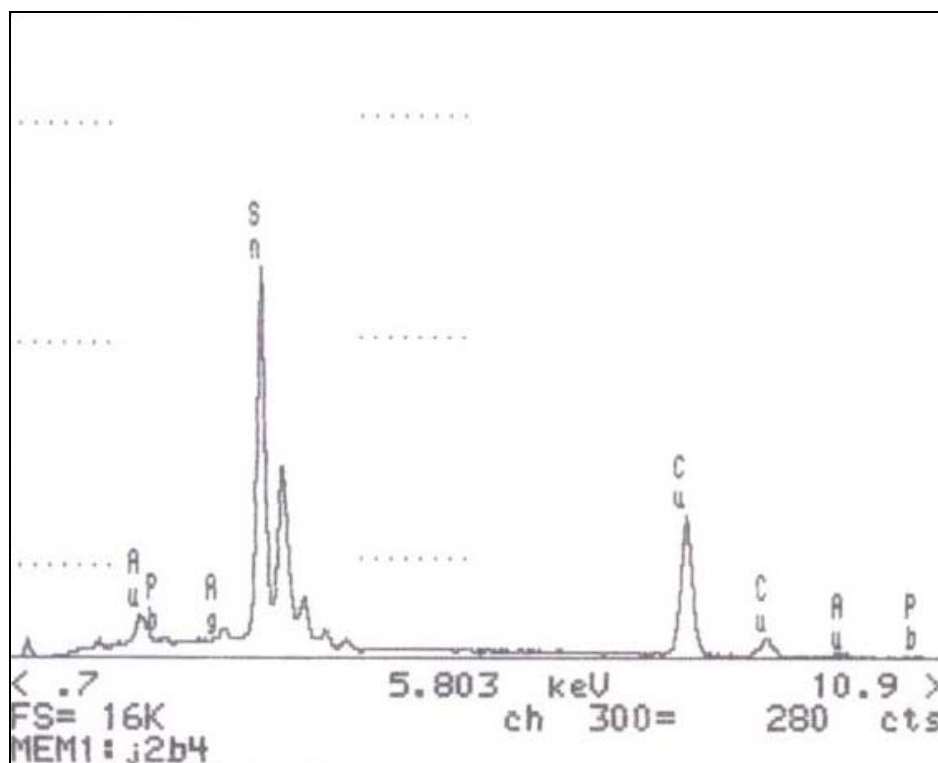


Figure 21: Position B in Figure 3, revealing the Cu_6Sn_5 globular phase.

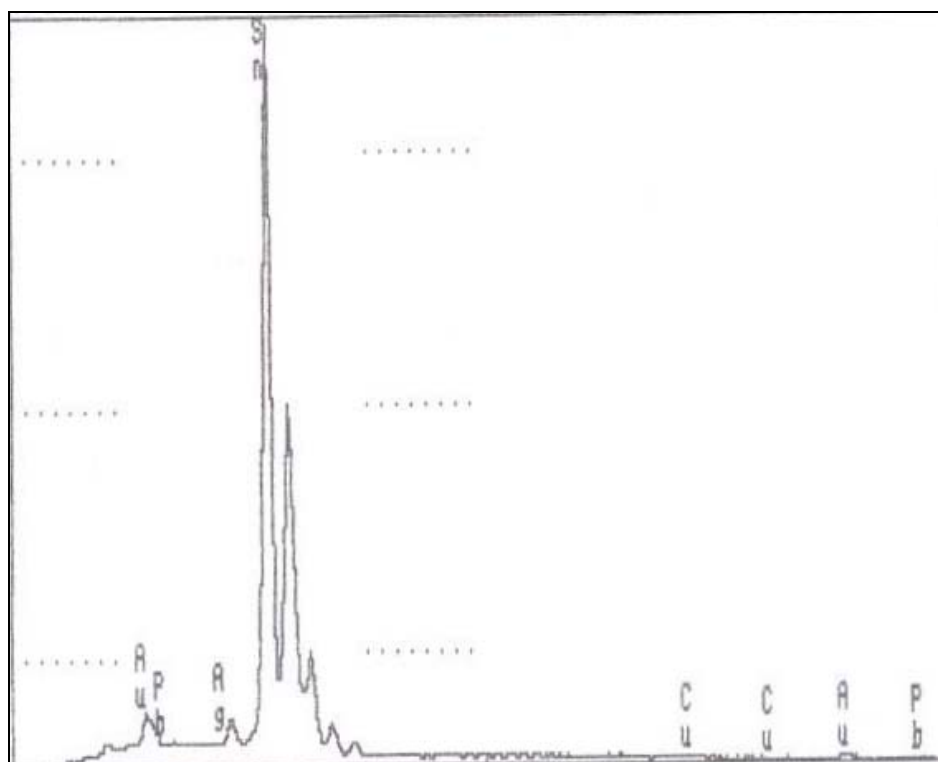


Figure 22: Position C in Figure 3, revealing Cu-rich globular phase

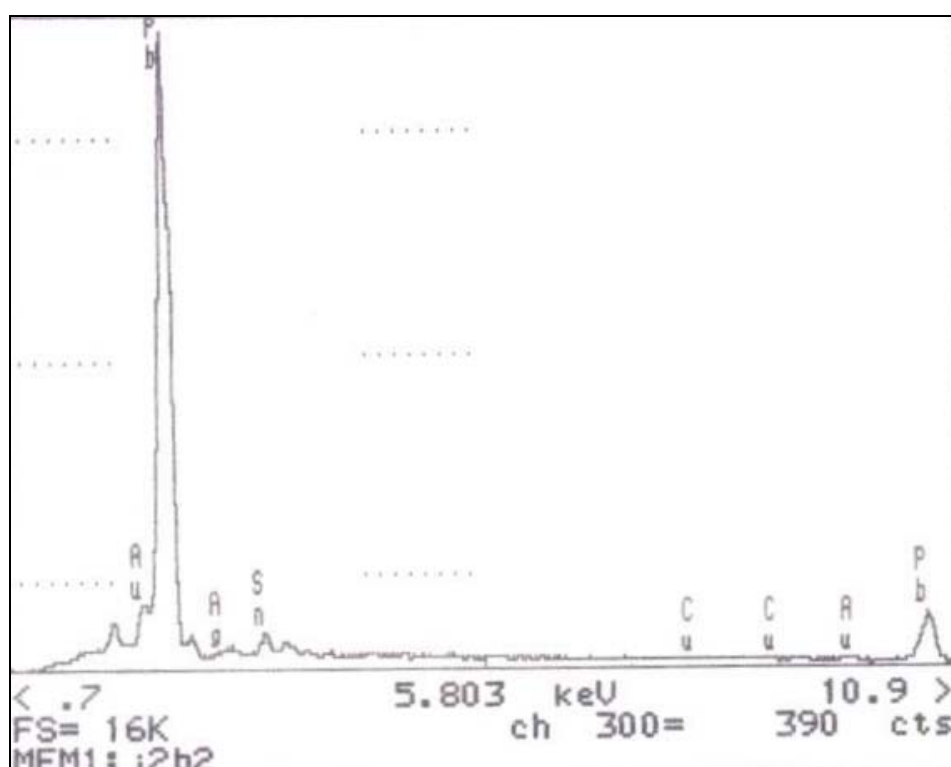


Figure 23: Position D in Figure 3, revealing Pb-rich lamellae phase.

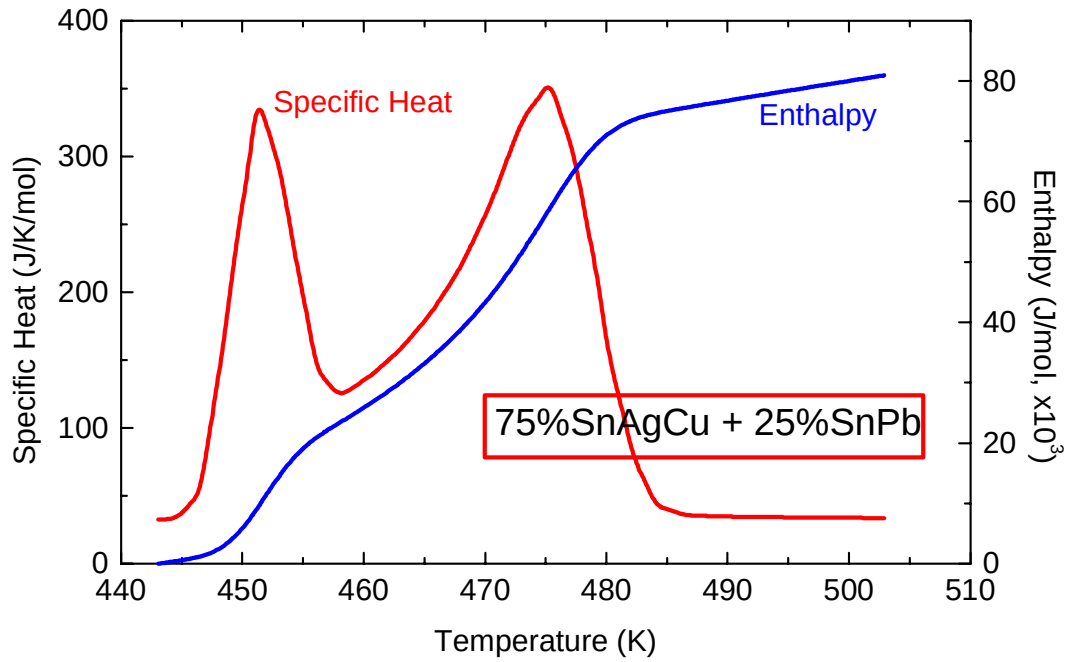
10 APPENDIX C: DSC AND ENTHALPY RESULTS

Figure 24. DSC and enthalpy results for solder A.

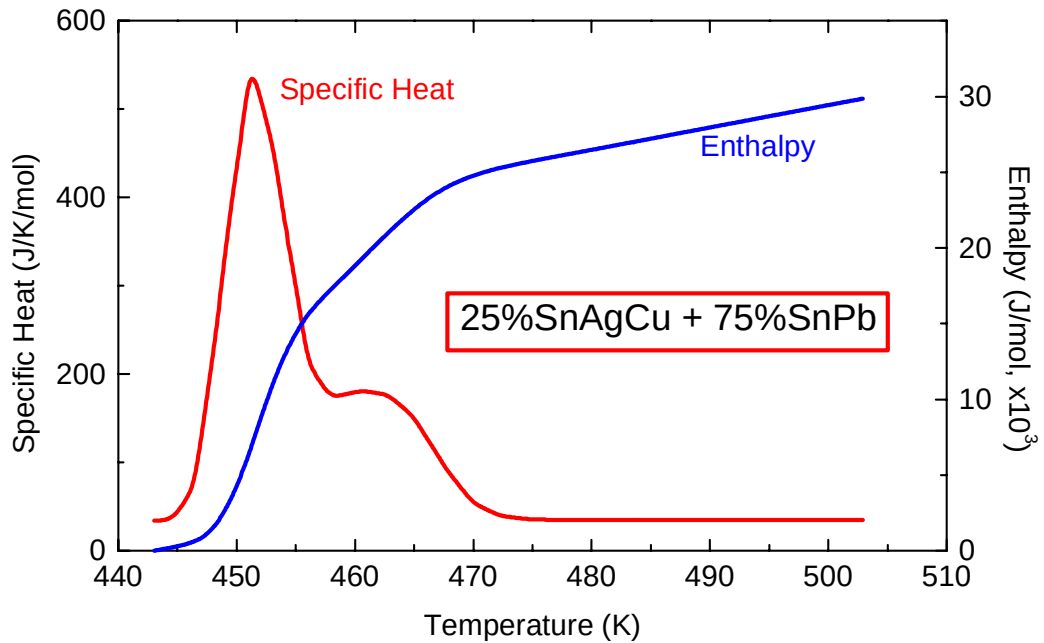


Figure 25. DSC and enthalpy results for solder B.