THE BI-SN EQUILIBRIUM PHASE DIAGRAM

Introduction

Equilibrium phase diagrams are one of the single most useful tools of a materials scientist and engineer. As maps of the temperature ranges and solubility limits of each known phase in the alloy system, including compounds, they are obviously useful to metal casters, heat treaters and ceramicists and are an invaluable tool in alloy design, in the development of high-temperature superconductors and in investigations of practically any temperature dependent property. To one who is familiar with how these diagrams are generated and especially to those who calculate phase diagrams they are also representations of a number of basic thermodynamic properties and in themselves contribute to a better understanding of engineering materials.

There are a number of methods available for establishing a phase diagram. One is x-ray diffraction. This technique allows one to make direct measurements of the changes in phase at temperature, allowing one to determine the transformation temperatures, identify the products of these transformations, and to study the details of the crystallographic aspects of phase transformations. Electron diffraction, done using a transmission electron microscope, can be used to obtain similar results, though it is limited to the analysis of very small regions of a specimen and elevated temperature electron microscopy can be very difficult and expensive. But the most commonly used methods are based on thermal analysis. These include differential scanning calorimetry (DSC) which measures the heat energy expelled or adsorbed by the sample as it undergoes phase transformations and differential thermal analysis (DTA) which carefully measures changes in heating or cooling behavior as compared to a reference material. Both of these can also be used to measure fundamental thermodynamic quantities such as heat capacity, enthalpy and entropy. Dilatometry is another thermal analysis technique which is widely used to measure the coefficient

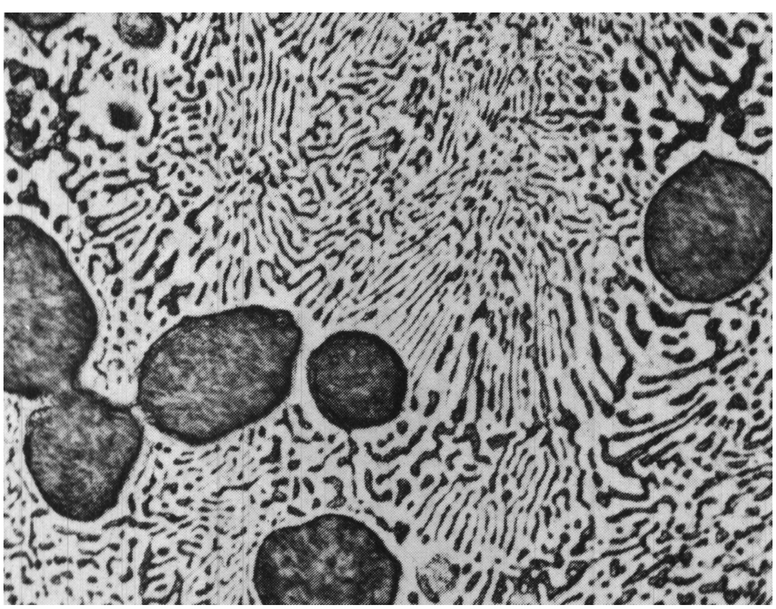

Figure 1. Half and half solder (Pb-50Sn), slowly solidified. The microstructure consists of dark grains of the lead-rich phase in a lamellar eutectic matrix consisting of dark lead-rich regions and light tin-rich regions. Magnification: approximately 550X [1].

of thermal expansion but can also determine a transformation temperature by detecting the rapid change in volume which accompanies a phase transformation. In general, one can devise any number of bulk and microanalytical methods for establishing a phase diagram by measuring any change in the sample which accompanies a phase transformation. In practice, the results of a number of techniques published by many authors are collected and carefully evaluated by the scientific community before they are made available for more general use and even then you may find differences in phase diagrams for the same system (compare figures 2 and 3).

The Bi-Sn system is a classic binary eutectic system and is a good example of a system which exhibits limited solid solubility and no intermediate compounds. Its phase diagram is very similar to that of the well known Pb/Sn system which provides us with a number of solders, including the 40/60 solder which is widely used in electrical applications. The simplicity of this type of system combined with the lower melting temperatures and lower toxicity of the Bi/Sn system makes it an ideal candidate for classroom experiments. As a low melting alloy Bi/Sn alloys are used in temperature overload devices and as solders in cases where the Pb/Sn solders are not suitable. For example, they may be used in wave soldering operations where surface mount components make direct contact with the molten metal, when the heat treatment of the metals being joined can be altered, when soldering other low melting point alloys such as pewter and when nearby solder joints might be compromised [2].

Objective

In this experiment the cooling curve method (similar to but simpler than DTA in that it does not employ a reference) is employed to determine the transformation temperatures for a set of Bi/Sn samples. These results are then used to construct an equilibrium phase diagram and this phase diagram is then used to determine the composition of a sample whose composition is unknown.

Preparation

Before actually starting the experiment you should stop to consider the suitability and performance of the instrumentation, certain aspects of the experimental procedure and to try to anticipate the experimental results. This will help ensure that the experiment goes well the first time. The following questions should get you started.

1. Sketch the equilibrium phase diagram for the Bi-Sn system.

2. What are the highest and lowest transformation temperatures you expect to measure when working with the 0, 10, 30, 50 and 100 weight percent Sn samples?

3. Estimate the value of Seebeck's coefficient for a K-type thermocouple for temperatures between room temperature and 300°C? Compare this to Seebeck's coefficient for a J-type thermocouple.

4. Combining questions 2 and 3, what are the lowest and highest voltages you will be measuring? What voltage resolution will you need to be able to resolve 1°C? What is the voltage resolution of your system?

5. When you put the thermocouple into the molten Bi/Sn mixture the thermocouple will cause the liquid to cool, possibly solidifying some of it before you can start measuring its cooling behavior. How do you plan to deal with this?

6. If your reference junction is not working properly, for instance if it is off or if the battery has died, how much error would you expect to see in your temperature measurements?

7. The molten samples will cool somewhat while you are transferring them from the heater to the insulated beaker where you will record its cooling behavior. How do you plan to deal with this?

8. Assuming you have done everything perfectly and the thermocouple is your only source of error, how large might this temperature error be?

9. If you don't weigh out your Bi and Sn perfectly you would expect the transformation temperatures you measure to differ from those in the established phase diagrams. How much error in weighing do you expect to see and how do you plan to deal with this error?

10. Indicate on your sketch (question 1) the sample compositions and transformation temperatures which will not be effected by errors in weighing out the Bi and Sn for your samples?

11. Assume your "unknown" sample has transformation temperatures of 139 and 195°C. Referring to your equilibrium phase diagram you can see that this fits two compositions. How would you determine the composition of this sample?

Materials

The raw materials you will be using to make your samples are generally reagent grade pure metals which are in either a granular or shot form. Note the type of metals used, their manufacturers, purities, form and part numbers.

Equipment

The following is a generic list of the types equipment that may be used in this experiment. Please make sure you have everything you need before starting the experiment and note exactly what type of equipment you will be using.

1. A heater capable of heating the test tubes to 400°C
2. Test tubes to hold the samples and tongs for handling the hot test tubes
3. Electronic balance with 0.01 gram sensitivity, weigh boats and two spoons
4. Insulated beakers (600 ml beakers filled with glass or ceramic wool)
5. Thermocouples with extension wires and reference junctions
6. Chart recorders or a DMM/scanner connected to a computer or another type of data acquisition system capable of measuring temperature using thermocouples
7. Containers for disposing of the samples and the test tubes

Safety

This experiment presents minor hazards for all students in the laboratory. Test tubes occasionally shatter so safety glasses should be worn from the moment the first specimen is heated until the last one is cool. The specimen materials themselves pose minor hazards due to their toxicity. These should be handled carefully and disposed of properly. (MSDS's for each chemical are available in the laboratory.) The most serious hazard is the possibility of being burned by the heater and the hot test tubes. The ceramic tubes which hold the test tubes are heated to nearly 400°C and the test tubes are often heated to above 300°C.

Chemical Hazards	There is a hazard associated with the minor toxicity of Sn and Bi. These materials should not be ingested and proper disposal methods should be used. Refer to the MSDS for each material.
Physical Hazards	Serious burns are possible. The ceramic heater tubes and the specimens in the test tubes are heated close to 400°C. The hot parts of the heater are labeled accordingly. Test tube clamps should be used when handling the hot specimens. The glass test tubes often break and spill the molten metal, especially when being reheated to remove the thermocouple. Safety glasses and closed toe shoes must be worn at all times.
Biohazards	None.
Radiation Hazards	None.
Protective Equipment	Recommended: laboratory aprons and long pants. Required: safety glasses or goggles. Normal eye-glasses are not acceptable. Open toed shoes will not be allowed.

Procedure

Examine the setup of the experimental equipment. Find out what each part does and how each part works. Make sure everything is working properly and if possible try a couple of dry runs of the experiment.

Weigh and mix the pure components to make samples of the specified compositions and the specified total weight. Transfer the pure components to a test tube and then cover and shake the test tube to thoroughly mix them. Finally, label each sample immediately to avoid mixing them up. Note that it might not be possible to weigh out these granular materials as precisely as you'd like so make sure you record the actual composition of each sample.

Carefully and gently melt each sample. Be careful to not overheat them or to heat them for too long as you might oxidize the sample or damage the test tube. On the other hand, make sure the sample has completely melted before removing it from the heater and while you don't want to overheat the sample you should heat it high enough above its liquidus that it doesn't start to solidify before you can start recording the cooling behavior.

Transfer the test tubes containing the melted samples to the insulated beakers and start recording the cooling behavior as soon as possible. Continue recording until you are sure that no additional phase transformations are expected. (Consult an established Bi/Sn phase diagram.) When done remelt the sample so that you can remove the thermocouple. Clean the thermocouple and dispose of the sample properly.

Results

A good way to start your analysis of the results is to make a brief qualitative review of the cooling curves. Which features do they all have in common, which ones are unique and what is the significance of each of these features? Are there different "types" of cooling curves and if so what type is the cooling curve for the "unknown" sample?

Moving on to the quantitative part of this section of the report, you will have to devise the best method for reliably and consistently determining the transformation temperatures. Perform this analysis, organize these results in a table and then plot these data points on an existing phase diagram. Note the similarities and differences and note the character and the magnitude of the experimental errors.

Once your own phase diagram is complete you should be able to determine the composition of the "unknown". In your report you will have to explain exactly how you did this and how much error you think there might be in your result.

Record any other interesting observations you may have made. These notes can be very helpful when writing your report.

Discussion

This experiment is straightforward and is essentially a duplication of the work of others. Your discussion will probably start out comparing your phase diagram to established phase diagrams (see figures 2 and 3) and you may even be able to say which phase diagram you'd put more stock in. Next, you may revisit the issue of experimental error before finally reviewing how the composition of the "unknown" was determined and telling the reader how confident he/she can be that your determination is correct. In general, you will have to convince the reader that you have done a good set of experiments, constructed a good equilibrium phase diagram and have demonstrated its usefulness by determining the composition of the "unknown" sample.

Conclusion

Formulate your own conclusions regarding the quality and utility of the phase diagram you have constructed. You may have also made other observations which merit a final comment. This is a good opportunity to make these comments.

References and Other Resources

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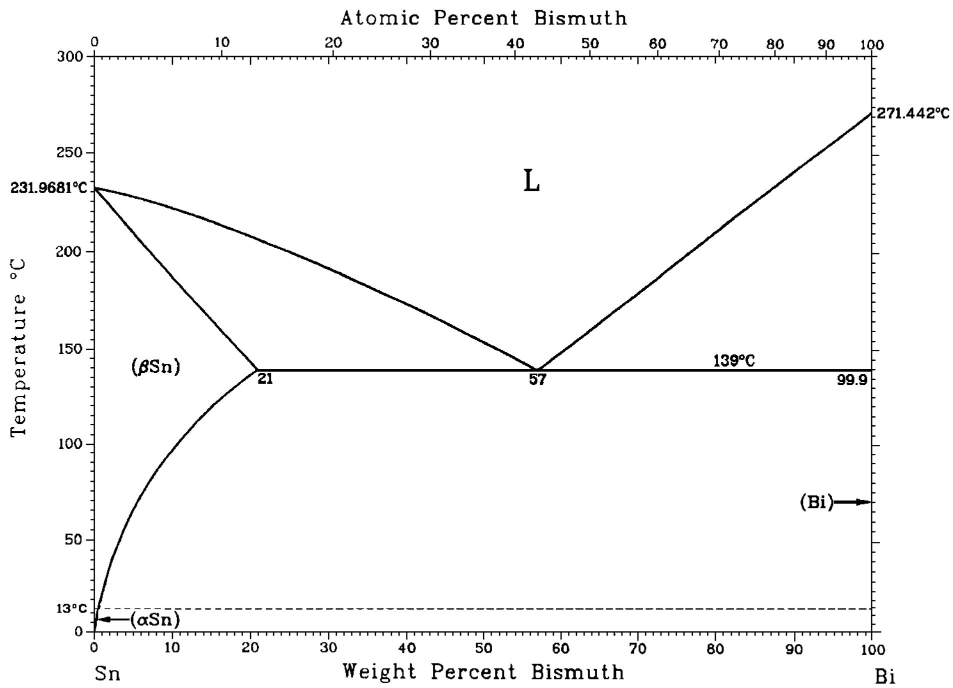

Figure 2. ASM Metals Handbook's equilibrium phase diagram for the Bi-Sn system [3].

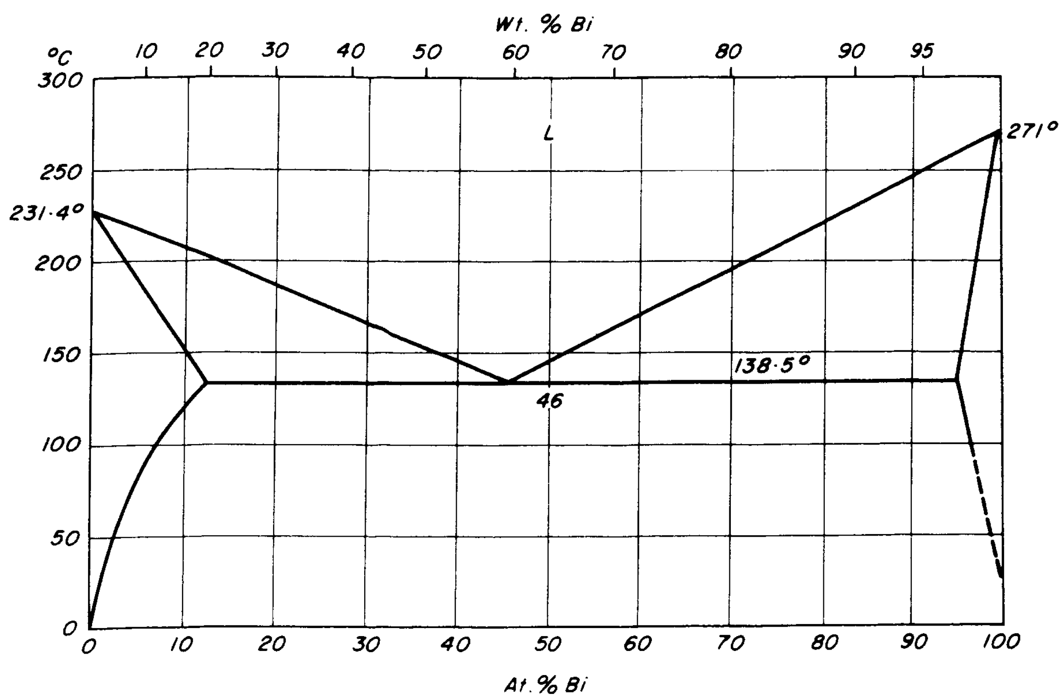

Figure 3. Smithells Metals Reference's equilibrium phase diagram for the Bi-Sn system [4].