Laboratory on Phase Equilibria with Optical Microscopy

Objective

The objective of this laboratory is for you to observe in real-time the microstructures that form during the solidification of a two-component alloy with a eutectic phase diagram.

Preparation

Read:

- Review sections of the textbook you used for MSE 182 or 201 that discusses eutectic phase diagrams and the microstructures that form during solidification.
- Read: A few pages from the introductory book by Smith on Compass
- Read: the introduction to the 1981 paper by Glicksman on Compass
- Read: "Thermodynamic description and unidirectional solidification of eutectic organic alloys: I. Succinonitrile-(d)camphor system" on Compass

Reference Values

- Review the phase diagram and be familiar with the temperatures at which transitions take place

Equipment and samples

- Optical microscope, Linkam hot-stage and controller (PE 94 or PE 95).
- Succinonitrile (SCN) and camphor mixture samples
- Hot plate
- Microscope slides and cover slips
- Computer, video camera, image acquisition and analysis software, and software for controlling the hot-stage (not necessary at one station)

Laboratory Safety: Phase Equilibrium

Required Personal Protective Equipment

- Safety glasses with side shields
- Long pants
- Closed toed shoes
- Chemically resistant gloves - (will be provided in the lab)

Safety Concerns

- Chemicals - potential for chemical exposure.
  - Several chemicals will be used during this lab experiment. Please read the safety data sheets for all chemicals (links included below, or available on Compass). Chemically resistant gloves should be worn while handling chemicals. Any spilled material should be cleaned up immediately.
    - Camphor MSDS
    - Succinonitrile MSDS
- Hot temperatures - potential for burns
  - A hot plate will be used to melt the mixture on a glass slide - keep hands away from the hot surface of the hot plate. This will reduce the risk of burns.
  - The slide may be hot when removing it from the hot plate. Use a pair of tweezers to move the slide until it cools down.
  - Keep all combustible material and flammable solvents away from the hot plate. This will reduce the risk of fire.
- Sharp glass - potential for cuts
  - Glass slides and slide covers can be sharp and cause cuts. Use caution when handling. If the slide breaks, please inform the lab instructor.

Waste Considerations

- Glass slides should be disposed of in the sharps container.
- Slides and spatulas can be cleaned with kim wipes and a solvent such as acetone or methanol. These wipes may be disposed of in the normal trash.

Introduction

Understanding and controlling the microstructures formed during the solidification of multi-component alloys is one of the fundamental concepts of Materials Science and Engineering. Essentially all metal alloys owe their strength to the microstructures that are created during solidification and heat treating. Details vary between systems but many aspects of the solidification of alloys are common to metals, ceramics, semiconductors, and small-molecule organics. In this lab, you will use a "transparent organic alloy" of succinonitrile (SCN) and camphor as a model system to observe the formation of microstructures in real-time in an optical microscope. Microscopy can be used to visually understand and predict the microstructural state of a specific alloy within a temperature range. SCN-camphor has a eutectic phase diagram with extremely small solubility in the solid state.

Phase diagrams are a convenient way to display graphically how changes in temperature, pressure, and composition can affect the phase transformations and microstructure of a particular alloy system. These diagrams are usually constructed under equilibrium conditions, where the system is given enough time (e.g., cooled slowly enough) to form the thermodynamically stable phases. These phases have the lowest free energy for the system. However, in real world applications, true equilibrium may never be reached. Thus, it is important to understand how changes in processing can affect the microstructures and properties of the alloy.

In this lab, samples of various compositions of SCN and camphor will be provided and observed under the microscope as they are melted and resolidified in the Linkam stage. Students will observe the phase transformations using the optical microscopes, looking for visible phase boundaries (dendrites typically). In addition, they will study how changes in cooling rate can affect the resulting microstructure.

Experimental Procedure

Part 1: Equilibrium phases in binary organic alloys

Using the phase diagram in the reference paper by Witusiewicz et al. as a guide, three alloys with eutectic, hypoeutectic and hypereutectic compositions have been prepared. Select **two** of these alloys to investigate, the eutectic and either the hypo- or hypereutectic composition. Heat the alloys to the liquid state (consult the phase diagram to determine an appropriate upper temperature limit) and cool the liquids slowly to room temperature. *Observe the phases in the various alloys as they are heated and cooled.*

From the phase changes, *determine the liquidus, solidus, and eutectic temperatures of the alloys*. Measuring the liquidus and solidus temperatures on both heating and cooling will help you separate the effects of heat transport and nucleation of the new phase from normal diffusion processes. Be aware that when a sample is heated or cooled, it will lag behind the set point of the hot stage. Consequently the sample is hotter than the set point temperature on a cooling step and cooler than the set point on heating. If you measure the phase transformation temperatures in both directions you can average the values to obtain a more reliable result. The slower you heat/cool the sample, the less the temperatures should lag behind the measured values, so the heating and cooling values should converge to the same value if you reduce the rate of temperature change enough. For this portion of the experiment, we recommend a cooling rate of **0.5°C/min** to simulate equilibrium conditions.

With the help of the image analysis software ImageJ, *analyze the fractions of each phase in the final microstructures (at room temperature) and compare your results with the predictions from the phase diagram*. Data will be shared between groups, so that all three compositions (eutectic, hypoeutectic and hypereutectic) can be analyzed in the report.

Part 2: Non-equilibrium microstructures of binary organic alloys

By increasing the cooling rate, you will limit the amount of time for atomic transport or diffusion so that the microstructures you observe will deviate from the equilibrium state. The non-equilibrium microstructures will be different from the equilibrium microstructures observed in Part 1 and will vary with the cooling rates. For this portion of the lab, rates of **1°C/min** and **10°C/min** are recommended, using the same alloys from Part 1. Observe the differences in the alloys with the eutectic, hypoeutectic and hypereutectic compositions (again sharing data where necessary). *Differences in microstructure can be quantified by measuring dendrite arm spacing (DAS) for all the alloys at the three different cooling rates.*

Procedures

- Use a small spatula to scrape a small amount of sample out of the sample vial - be sure to note the concentrations of each component. Make sure the spatula is clean to avoid cross-contamination.
- Transfer a small amount of the sample onto a microscope slide
- Place the slide on the hot plate and turn the heat dial on so that the sample will melt on the slide
- Once melted, place a cover slip over the sample. The liquid sample should cover the slide surface seen through the Linkam viewing port.
- Transfer the slide to the Linkam Stage
- First cool the sample down to room temperature in order to solidify it completely
- Program the Linkam stage to heat at your desired rate in order to melt the samples
    - Heat quickly to 5°C above the expected liquidus temperature. Hold at this temperature for at least 2 minutes.
    - Cool the sample at the specified rate (0.5°C/min, 1°C/min, or 10°C/min) to 32-35°C.
    - Hold the temperature below the eutectic temperature for 10 minutes.
    - Rapidly cool the sample down to room temperature. Hold at 22°C for about 1 minute.
- Observe and record the transition temperatures and microstructures that form.

Instrument specific procedures

Reflected Light Microscope

This experiment utilizes a reflected light microscope. We will be using the 10x objective to observe the melting and solidification of materials, as controlled by a hot-stage. Remember to focus the image by first lowering the stage and then slowly raising it toward the objective, always paying close attention to the position of the hot-stage relative to the objective. DO NOT CRASH THE OBJECTIVE LENS INTO THE HOT STAGE. Coarse tuning knob (larger) should be used first, and then fine tuning. Sample position can be adjusted using the stage controls, the vertical rod with two knobs.

Infinity© Camera

A camera is attached to each microscope, which can be used to view the image on the computer stations. The program INFINITY ANALYZE can be used to view the image, adjust image properties, and record the image. Scale bars can be added by first calibrating the camera with a stage micrometer, and then selecting Micrometer under the Annotation tab. Measurements of linear distance, angle, radius and more can be done under the Measurement tab.

Linkam hot-stage

A hot-stage is used to melt and solidify the alloys of interest under programmable temperature control. The hot-stages hold a standard-sized microscope slide, on which you will place your sample and cover slip. After the sample is in place, the hot-stage can be placed on the microscope stage with the glass window underneath the chosen objective lens. The slide position in the hot-stage can be adjusted using the knobs on two sides of the hot-stage. The long working distance restriction imposed by the hot-stage limits the possible objectives to 10 and 20x.

Linksys32 software

Linksys32 is the program which controls the temperature profile for the hot-stage. After turning on the control box and water chiller and opening the program, click File/ Connect to establish communications between the computer and the control box. Temperature control can be done in real-time by manipulating the values in the boxes, or a temperature profile can be set up.

NOTE: One station has a PE-95 controller instead of a PE-94, which does not require Linksys 32 and operates via a touchscreen interface instead. Similar temperature profiles can be setup using the interface.