3.014 MATERIALS LABORATORY
MODULE – ALPHA 3
October 24 – October 28, 2005
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DIFFERENTIAL SCANNING CALORIMETRY STUDY OF SUPERCOOLED METALS

OBJECTIVE:

- Measure Heat Flow vs. Temperature profiles (Heat-Cool cycle) of metals with low melting temperatures: Indium, tin, lead and lead 33 wt% -tin 67 wt% alloy, using differential scanning calorimetry (DSC).
- Evaluate the extent of supercooling (or undercooling) in these metals.
- Evaluate the thermodynamic quantities (**Specific Heat Capacity, Melting Temperature, Enthalpy of Melting, Entropy of Melting**) of these metals.

INTRODUCTION:

When a material in the liquid (or molten) phase is cooled well below its equilibrium melting temperature without solidifying (or crystallizing), the material is said to be in a supercooled or undercooled state. [1,,2,3] The degree of supercooling, ΔT measures this offset in solidifying temperature from the material's normal melting point, T_m. The supercooling state results because of a large barrier to the formation of an ordered crystalline phase. [3,4]

Supercooling of metals was first observed in 1950 by David Turnbull and Robert Cech. [1] Some metals are observed to remain in the metastable, undercooled state for as much as hundreds of degrees below their normal melting temperature before they spontaneously solidify. For example, a maximum undercooling, ΔT of 80 ˚C, 227 ˚C and 332˚C has been reported for lead, silver and platinum , respectively.[5]

How a material solidifies is important in industrial processes, such as metal casting.[5] The thermal properties, hence effects of supercooling of lead-tin (Pb37 wt%-Sn63 wt%) solder alloy has been investigated for its significance in electronics industry. [6] Supercooled salts of phase change materials have useful applications as thermal storage systems (heating pads , winter gloves).[7] [see Module-beta 1 notes from Lab week 1]

As a metal is cooled below its melting temperature, several stages occur, “formation of a nuclei”, “growth of nuclei into crystals”, and “grain formation”. [You will learn next semester]. According to classical concepts, the supercooled state is caused by a high energy barrier for the formation of crystal nuclei of critical size which can then grow into stable crystal phase. [2,3,5] Usually, it is not easy to supercool liquid metals since dust and other impurities in the liquid, or defects in the container holding the liquid, can reduce this barrier and initiate nucleation, changing the liquid to a solid phase near the equilibrium melting temperature. [2,4,8] For this reason, supercooling experiments are usually conducted by levitating metals of high purity, electrostatically or electromagnetically or as suspensions in oil. Specimens in the form of a tiny piece or microspheres or liquid drops are typically used. With the reduction in size, the number of defects initiating the crystallization is expected to decrease favoring the liquid to supercool. [4,8,9]

Recent X-ray diffraction experiments on levitated drop of metal confirm the previously hypothesized structural differences in the undercooled liquid phase and the ordered crystalline phase, and its effect on the barrier to solidification. [3,4,9] The results confirm an icosohedral order for the undercooled liquid phase, a structure depicted in figure 1 and 2, possessing a five-fold symmetry (similar to that observed in some quasi-crystals and metallic glasses). As the metal liquid is cooled, it first forms a noncrystalline icosohedron phase and then a stable solid crystalline phase. The barrier to solidification is attributed to the incompatibility of these structural orders in the undercooled metastable phase and the stable ordered solid phase.

In this experiment, you will test if the selected samples of indium (In), tin (Sn), lead (Pb) and lead-tin alloy supercool, and if the degree of supercooling can be measured using Differential Scanning Calorimetry (DSC) technique. Also, the thermodynamic properties of these metals will be evaluated.

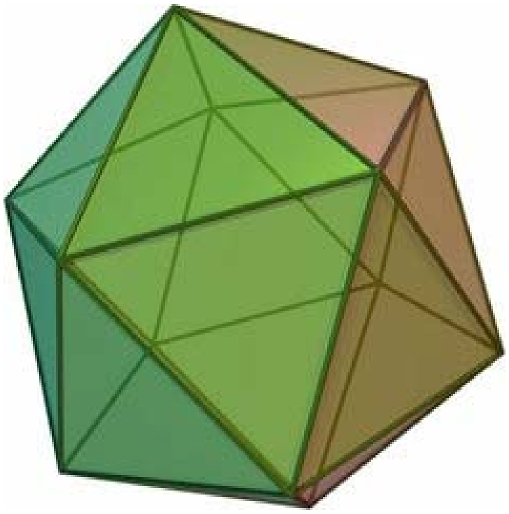

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Figure 1: An icosohedron, a geometry with 20 triangular faces
Figure adopted from, http://en.wikipedia.org/wiki/Icosahedron

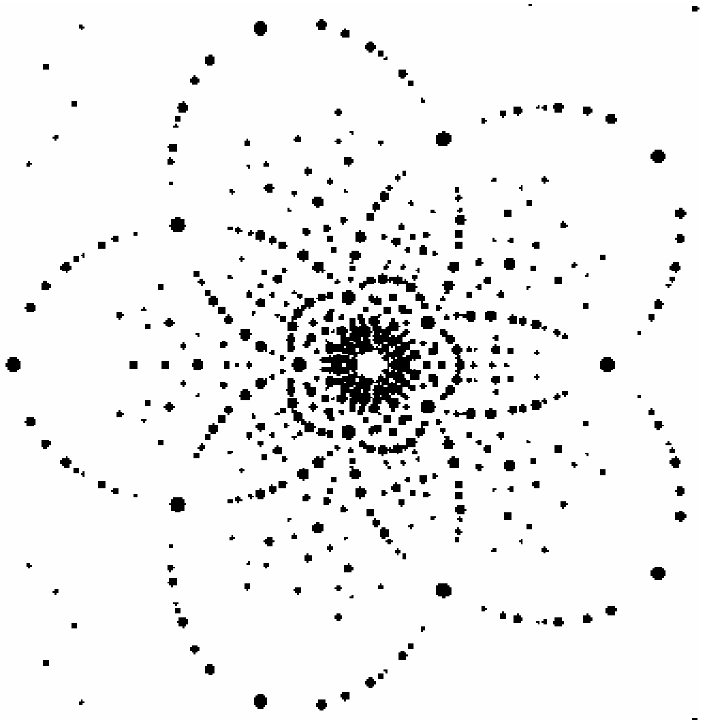

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Figure 2: A simulation for a ***Laue pattern*** (X-ray) from an icosahedral quasicrystal showing five-fold symmetry.
Figure adopted from**, http://www.jcrystal.com/steffenweber/qc.html**

MATERIALS:

Indium shots, Alfa Aesar, #11027, 99.99%
Tin granules, Alfa Aesar, #36691, 99.99%
Tin wire, Merway Inc., #125
Lead granules, Alfa Aesar, 36227, 99.5%
Lead 37% -Tin 63% alloy solder wire, Kester, #24-6337

EXPERIMENTAL TECHNIQUE:

DIFFERENTIAL SCANNING CALORIMETRY [DSC] – TA INSTRUMENTS – MODEL Q100

- TA Instruments Q-series Manual on DSC[10]
- "Experimental Evaluation Of Procedures For Heat Capacity Measurements By Differential Scanning Calorimetry", K.L.RamKumar, M.K.Saxena, and S. B. Deb, Journal of Thermal Analysis and Calorimetry, vol. 66 (2001) 387-397]

DSC is a thermal analysis technique useful for measuring thermal and thermodynamic properties of materials such as, the specific heat, melting and boiling points, glass transitions in amorphous/semi-crystalline materials, heats of fusion, reaction kinetics etc. The technique measures the temperature and the heat flow (in desired units, mW, W/g etc.) corresponding to the thermal performance of materials, both as a function of time, and temperature.

The TA Instruments DSC is a "HEAT FLUX" type system where the differential heat flux between a reference (e.g., sealed empty Aluminum pan) and a sample (encapsulated in a similar pan) is measured. The reference and the sample pans are placed on separate, but identical stages on a thermoelectric sensor platform surrounded by a furnace. As the temperature of the furnace is changed (usually by heating at a linear rate), heat is transferred to the sample and reference through the thermoelectric platform. The heat flow difference between the sample and the reference is then measured by measuring the temperature difference between them using thermocouples attached to the respective stages.

The DSC provides qualitative and quantitative information on endothermic / heat absorption (e.g., melting) , exothermic / heat releasing (e.g., solidification or fusion) processes of materials. These processes display sharp deviation from the steady state thermal profile, and exhibit peaks and valleys in a DSC thermogram (Heat flow vs. Temperature profile). The latent heat of melting or fusion can then be obtained from the area enclosed within the peak or valley. The shift in the peak locations corresponding to melting temperature and solidification temperature measures the degree of supercooling.

The glass transition is characterized by a steady change in the slope of the heat flow vs. temperature profile, with a corresponding change in the heat capacity of the material.

Some factors that may affect the DSC measurements are :

- Sample positioning on the DSC stage
  (variations in baseline)
- Structure and mass of the sample
  (proper thermal contact)
- Heating rate
  (Trade-off between sample attaining thermal equilibrium and data acquisition times. A fast heating rate may minimize the data acquisition time compromising salient features of the material property)

SAMPLE PREPARATION FOR DIFFERENTIAL SCANNING CALORIMETRY [DSC] MEASUREMENTS:

Weigh a clean granule or a tiny piece of the metal in a NORMAL aluminum DSC pan.
Crimp the pan with the lid.
(Clean the samples with isopropyl or ethyl alcohol)

EXPERIMENTAL PROCEDURE:

SPECIFIC HEAT CAPACITY MEASUREMENTS:

The guidelines for heat capacity measurements provided by TA Instruments (**see handout**)[10] will be followed.
These guidelines are based on ASTM Method, D3947 – 80. [11]
(with modifications* due to time constraints)

1. Obtain a baseline (zero line) thermal profile (Heat Flow vs. Temperature) with empty, identical (equal mass) aluminum pans placed on the reference and the sample stages, respectively.

   The aluminum pan on the reference pan must be **crimped**.
   The pan on the sample stage is left uncrimped for later use.

   The baseline scan corrects for any asymmetry in heat flow of the system.

   SCAN conditions:

   - Set point temperature: 40 ˚C

   - Mass of the sample:
     Input, 0 (ZERO) for the mass of the empty pan in baseline scan

   - Scan Mode: RAMP

Equilibrate at 10 ˚ C
Heating rate: @ 10˚ C / min scan to desired temperature
(The final temperature above the metal's melting temperature)

Note: Each scan may take at least 30 - 45 minutes.

* Ideally, an independent baseline profile must be obtained for each sample using the same pan in which it will be placed. However, in the present study, only one baseline scan will be performed for all samples, assuming identical mass or volume for all the pans (select pans and lids of similar masses).
Leave the pan on the reference stage undisturbed for the remaining measurements.

2. Obtain a thermal profile with a calibration standard (e.g. Sapphire) using the same scan conditions as in step 1.
   Provides a calibration factor that translates the measured Heat Flow units (in mW) to Heat Capacity units (J/g˚C).

   Place the crimped pan containing the calibration standard (sapphire, **mass = 25.68 mg**) on the sample stage.

3. Obtain thermal profiles of the metal samples using same scan conditions as in steps 1 and 2.
   Enter the weighed amount for each sample in mg.

   Place each crimped pan containing the weighed amounts of sample on the sample stage.

4. Subtract the baseline data from the sample and the sapphire data, prior to analysis.
   [Remember to change the Heat Flow (y-axis) units to mW, before subtracting the data, to ensure identical units for the sample and baseline profiles]

5. Analyze the data as explained below.

MELTING and SOLIDIFICATION CHARACTERISTICS:

SCAN conditions:

- Set point temperature: 40 ˚C
- Mass of the sample:
- Scan Mode:

Heat-Cool cycle
Temperature range: sample dependent
Scan rate: 10 ˚C / min (5 ˚C/ min - time permitting)

Place each crimped pan containing the weighed amounts of sample on the sample stage.

ANALYSIS:

SPECIFIC HEAT MEASUREMENT:

[see hand out: Quantitative Analysis – TA Instruments] [10]

1. Calculate the specific heat (C_p) of each metal and alloy sample @ 25 C (solid phase) and a temperature above T_m (liquid phase)

$$C_p \text{ (sample)} = \frac{C_p \text{ (sapphire)} \times m \text{ (sapphire)} \times \Delta H \text{ (sample)}}{\Delta H \text{ (sapphire)} \times m \text{ (sample)}}$$

Where,

ΔH is the heat flow (in mW) at a given temperature, obtained from the baseline subtracted plot of Heat Flow (mW) vs. Temperature for each sample, and for sapphire.

m is the mass of each sample, and sapphire, in mg

Note:

- The table in the hand-out [10] provides the C_p (sapphire) values as a function of temperature. Estimate the Cp values at the desired temperature.
- The known C_p (sapphire) values at a given temperature, translates the measured Heat Flow (in units of mW) to Heat Capacity units (J / g ˚C).
- The above equation is obtained by writing the equation for Cp, given in step 5 of reference 10, explicitly for the sample, and sapphire, and dividing the two equations. (i.e., the ratio of specific heat capacities for the sample and sapphire).

2. Compare your results at 25˚ C with standard values for each of the metals

MELTING AND SOLIDIFICATION CHARACTERISTICS:

1. Use the Universal Analysis software of the DSC and the "Peak Integration" routine to determine from the melting profile, the Melting Temperature, T_m and the Enthalpy of Melting, ΔH_m for each metal and alloy sample. Compare your results with standard values for the metals.

2. Using the values for T_m and ΔH_m, calculate the Entropy of Melting.

3. Use the Universal Analysis software of the DSC and the "Peak Integration" routine to determine from the cooling profile, the Solidification Temperature, T_s and the Enthalpy of freezing, ΔH_s for each metal and alloy sample.

4. Evaluate the degree of supercooling, ΔT, from the Heat-Cool thermal profiles. Present the ratio, $\Delta T / Tm$.

5. Calculate $(\Delta H_m - \Delta H_s)$ using the measured values of C_p and ΔT. Compare with the values estimated in Q.3, above.

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