

# 316-1 Labs

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### Laboratory 1: Diffusion in Substitutional Cu-Ni Alloys

#### Objectives

- To observe diffusion in a Cu-Ni diffusion couple.
- To determine if these observations are consistent with a composition-dependent interdiffusion coefficient, expected for diffusion in substitutional alloys.
- To begin to model the diffusion process using MATLAB.

#### Introduction

In the case of pack-carburization, we were able to make the assumption that diffusivity of carbon in iron was independent of composition. For substitutional alloys, this is not the case. The interdiffusion coefficient in this case is composition dependent and related to the intrinsic diffusion coefficients as follows:

$$\tilde{D} = X_a D_b + X_b D_a$$

In addition, in situations where  $D_a$  and  $D_b$  differ from one another, there will be a net vacancy flux in the material, giving rise to the motion of an inert set of markers that can be observed experimentally.

## Samples

Samples have been prepared using two techniques:

1. electroplating of nickel layers onto copper, and
2. welding Ni-Cu sandwich layers.

In both cases, Mo wires were placed at the interface, to mark the position of the original interface; however in the case of the electroplated samples, these wires sometimes shifted away from the surface during plating. After electroplating/ welding, the samples were sealed in evacuated quartz tubes to prevent oxidation, and annealed at 1000°C for 4, 16, and 72 hours.

**Laboratory Procedure** Refer to the class notes in addition to the paper describing the background and history of the Kirkendall effect [1]. Look at the Cu-Ni samples (annealed at 4, 16 and 72 hours at 1000 °C) under the optical microscope. Note that there are two types of sample: 1) copper strips wound with Mo wire which were nickel-electroplated and 2) a welded "sandwich" of nickel with outer copper layers and rolled molybdenum "marker wires" at the interface. Note that in (1) the Mo was not secured to the copper strip well-enough to mark the original interface (this will be obvious in your observations). In (2) you will find enough pairs of wires that are nearly across from each other to measure the distance between markers as a function of time at elevated temperature. (Unfortunately, the weld broke on the unannealed (time = 0) samples; but you should be able to assess the three remaining samples quantitatively or at least semi-quantitatively. Include these measurements with your other observations, as well as a discussion of what you expected. Discuss whether or not your observations and measurements are consistent with the Kirkendall effect. In future exercises we will be comparing these diffusion profiles to what we would expect from published values of the relevant diffusion coefficients. For now document your in-class observations, including well labeled sketches and micrographs.

## Laboratory 2: Recovery, Recrystallization and Grain Growth in Cold Worked 70/30 Brass

### Objectives

To observe the phenomena of recovery, recrystallization and grain growth. To understand the effect of processing on microstructure, specifically the effect of amount of cold-work on recrystallization and final grain size. To understand the time dependence of grain growth. To understand the predictions of the Hall-Petch relationship.

### General Procedure: Week 1

You will be provided with brass (70%Cu, 30% Zn) that has been heated to 700° C for six hours, from the as-received state and then rolled to reductions of ~ 15% and ~ 30%, as well as some brass that has not yet been rolled. Your groups will cold-roll samples to similar reductions for the next group. The specified amount of cold-work will be introduced using the rolling mill.

1. Measure the thickness and the Rockwell hardness of your as-received and rolled samples. Choose an appropriate Rockwell scale over which you can anticipate measuring your sample after it is rolled – then subsequently annealed. Always check to make sure the load and indenter size correspond to the correct scale. Use a standard to check the tester.
2. As a group, roll two samples, using the rolling mill, one to a reduction of ~ 30-40%, a second to a lesser reduction, e.g. 15-20%. Anticipate the target thickness before you begin rolling. Calculate target thicknesses for each reduction, assuming width does not change with rolling. Percent reduction (or percent coldwork) is defined as:

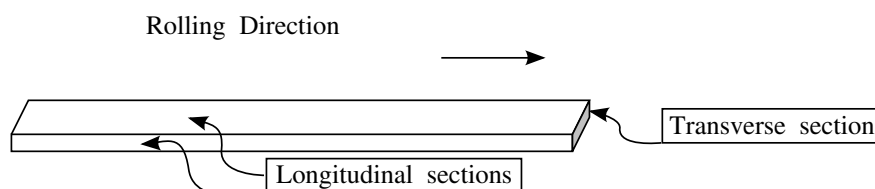
$$\%CW = \frac{A_0 - A_d}{A_d} \times 100 \quad (1)$$

which may be re-written for this lab:

$$\%CW = \frac{t_0 - t_d}{t_d} \times 100 \quad (2)$$

where  $t_0$  is the starting thickness and  $t_d$  is the final thickness. Set aside for the next group.

1. Re-measure hardness after rolling. (Make sure to measure a flat region. The sample should not deflect when the indenter is applied.)
2. Section the rolled samples into about 8 pieces (~ 1cm long). Note that we will be interested in observing the transverse sections, defined in the figure below. Set aside a time = 0 sample; each of the other 1 cm long “coupons” will be annealed at a specified time at the temperature assigned to your group



3. Record the temperature assigned to your group.  $T = \_\_\_ \text{ degrees C.}$
4. samples that have been annealed from 2 minutes, 8 minutes, 32 minutes...up to a week. You will be measuring and recording Rockwell hardness on each of these samples, then mounting them for polishing and etching.
5. After reserving the time = 0 sample, place the remaining samples in the furnace assigned to your lab group. (All samples of both reductions, except  $t=0$ , should be annealed at the SAME TEMPERATURE)

\*\*\*Suggest (the entire group's) annealing conditions by reviewing information available in the Metals Handbook, and by discussion with your lab mates & instructor. You want to achieve conditions under which you will observe partial to total recrystallization. Consider how you will need to vary the conditions to test the Johnson-Avrami-Mehl equation.

### General Procedure: Week 2

1. Make sure you have measured the Rockwell hardness of each annealed sample. Note that you should try to take all your hardness readings on the same scale.
2. Mount transverse cross-sections of each of the annealed samples, along with an unannealed piece in an acrylic mount for polishing. Follow the instructions for the auto-polisher. Wash your sample carefully and ultrasonic between each step to avoid contaminating the wheels. (These are soft samples; it will be difficult to remove the scratches that are introduced by such contamination!)
3. Etch to reveal grains. (Be careful; the different reductions and different temperatures of annealing may result in different etch rates.) Record a photomicrograph of each sample at an appropriate magnification.
4. From your micrographs, calculate the volume fraction of recrystallized material, and the grain size of samples that are completely recrystallized.
5. Measure the Vickers hardness of each sample (three indents, minimum, on each sample.)

### In-Lab Questions DUE at the Beginning of Week 2:

Rolling, hardness testing and cutting will take some time. If you are waiting you may use time in lab to answer the following. Make sure you define all terms and cite sources:

1. What equation describes the rate of grain growth?
2. Refer to Chapter 3 of Shewmon and summarize the "Engineering Laws of Recrystallization" relevant to this experiment. (You may summarize all – then determine which you might be able to test vs. not able to test.)
3. What equation describes the volume fraction of material recrystallized with time?
4. How can the rate of recrystallization at a given temperature be determined?
5. What is the Hall-Petch equation? Discuss the equation and any limitations.

### Final Deliverable - Group PowerPoint Presentation

Your presentation will be judged on content, delivery (presentation style), neatness, completeness. You must submit a hardcopy of your presentation slides. Imagine you are presenting this to Prof. Voorhees and other MSE students who were not in lab; they are familiar with terms like grain size and hardness, but do not know the details of your sample preparation and what you are testing (i.e. which of the Engineering laws of Recrystallization you were able to test.) Length: 12 minutes. Each group member must participate.

Due: one week after completing in-class measurements.

1. Refer to Chapter 3 of Shewmon; discuss whether or not the class data substantiates the “Engineering Laws of Recrystallization,” i.e. how do hardness, grain size, volume fraction of recrystallized material vary with the amount of cold-rolling, and time of anneal? Plot hardness (Rockwell is OK, here) as a function of annealing time for both reductions, including time = 0 values. Explain changes in hardness by comparison with micrographs.
2. Estimate the recrystallization rate for your group’s annealing temperature: Rate = 1/(time for volume fraction transformed = 0.5).

Note: We will try to use the information from different groups to compare recrystallization as a function of temperature. If you have enough points (this is unlikely), you may be able to fit the Avrami (JMAK) equation:

$$y \text{ (fraction recrystallized)} = 1 - \exp(-kt^n) \quad (3)$$

3. Make sure you use actual – not target reductions – when discussing your results. Double-check that the reduction is, for example, 40%, not 70%.
4. For samples in which complete recrystallization was observed – does the Hall-Petch relationship hold? Assume that hardness is proportional to yield strength (see next page). The Hall Petch equation states that the yield stress,  $\sigma_y$ , is increases linearly with  $d^{-1/2}$ , where  $d$  is the average grain size:

$$\sigma_y = \sigma_0 + \frac{k_y}{d^{1/2}} \quad (4)$$

where  $\sigma_0$  and  $k_y$  are constants for a given material. Note that you do not have to confine comparisons to a single recrystallization; use all the samples available that have recrystallized. (It tends not to be valid for very large or very small grains.)

5. For completely recrystallized samples, is normal grain growth observed? Measure grain sizes for recrystallized material at a given reduction and determine the exponent for grain growth as a function of annealing time at a given temperature:

$$d^n - d_0^n = Kt \quad (5)$$

Solve to see if  $n$  is greater than or equal to 2, as expected. Note that at the start of recrystallization, the grain size is infinitesimally small.

**Heyn Procedure for counting lineal intercept length:[2]**

1. Estimate the average grain size by counting, on a micrograph, screen or the specimen itself, the number of grains intercepted by one or more straight lines sufficiently long to yield at least 50 intercepts. Select the magnification such that this can be done in a single field.
2. Make counts on 3-5 blindly selected, widely separated fields.
3. Use a factor of 1.5 to determine the average grain size from the lineal intercept length.

**Hall-Petch determination:**

1. Measure Vickers hardness.
2. Use hardness and grain size to determine if the Hall-Petch relationship holds true for your data. (Plot HV vs.  $1/\sqrt{d}$ )
3. You can use Vickers hardness to calculate the Yield strength of brass. Assume 1/3 of the applied load in a Vickers Hardness test plastically deforms the sample and use the appropriate conversion factor ( $CF$ ) to convert to MPa:

$$\sigma_y = \frac{HV \text{ (kg/mm}^2\text{)}}{3} \times CF$$

Q – Are your values of yield strength within a reasonable range? Compare to typical values (Metals Handbook)

**Empirical relationship between Rockwell B and Vickers hardness ( $\text{kg/mm}^2$ ).** Note that it is best to measure the Vickers hardness directly. The following relationship between the Vickers hardness ( $HV$ ) and Rockwell B hardness ( $R_b$ ) is obtained from ASTM Standard E140 (table 4, Conversion data for Cartridge brass), Annual Book of ASTM Standards, volume 3.01, 1989:

$$HV = 0.002R_b^3 - 0.0092R_b^2 + 0.8163R_b + 52.865 \quad (6)$$

## Laboratory 3: Surface Energy and Contact Angles

### Objectives

- To understand what aspects of liquid behavior are determined by surface and interfacial energies.
- To understand how contact angles are used to characterize material surfaces.

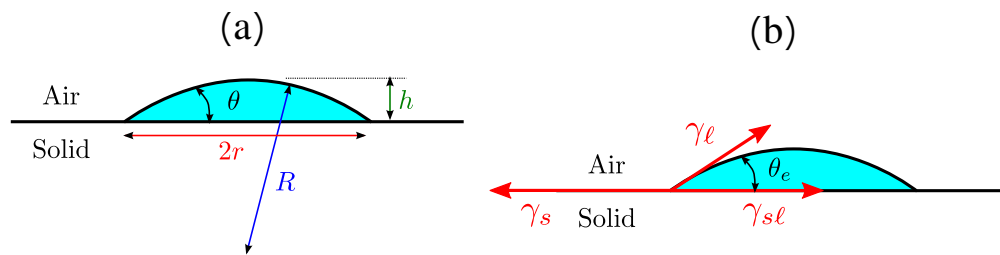
### Introduction

The properties of solid surfaces are often probed by measuring the ability of liquids to spread over the surface of a material. The relevant property is the contact angle,  $\theta$ , illustrated in Figure 1a. If the droplet is small enough so that it is not affected by gravity, the radius of curvature,  $R$ , of the droplet is uniform, and shape of the droplet is a spherical cap, *i.e.*, the portion of a sphere that exists above a specified plane. The relationship between the droplet height,  $h$ , the basal radius of the droplet,  $r$ , and the contact angle in this situation is as follows:

$$\tan\left(\frac{\theta}{2}\right) = h/r \quad (7)$$

At equilibrium, a horizontal force balance at the periphery of the object gives the following expression for the equilibrium contact angle,  $\theta_e$  and the relevant surface and interfacial energies (Figure 1b):

$$\gamma_s = \gamma_{sl} + \gamma_\ell \cos \theta_e \quad (8)$$

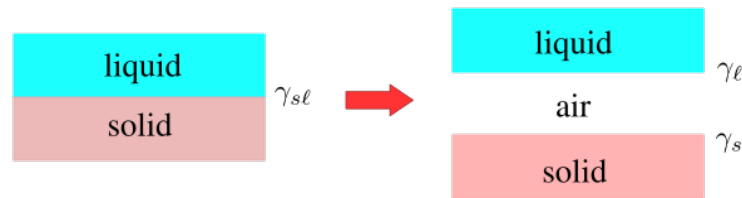


**Figure 1:** a) Geometric parameters characterizing the shape of a small liquid droplet on a solid surface. The b) Force equilibrium illustrating the origins of Eq. 8.

It is often useful to rewrite Eq. 8 in terms of the thermodynamic work of adhesion,  $W_{adh}$ , which describes the energy required to remove the liquid from the solid surface, replacing the solid/liquid interface with a liquid/air interface and a air/solid interface (see Figure 2):

$$W_{adh} = \gamma_s + \gamma_\ell - \gamma_{sl} \quad (9)$$

Here  $\gamma_s$  is the solid surface free energy,  $\gamma_\ell$  is the liquid surface free energy and  $\gamma_{sl}$  is the solid/liquid interfacial free energy. Note that for liquids, the surface tension and the surface free energy are identical to one another, so we refer to  $\gamma_\ell$  as either the liquid surface tension or surface free energy.



**Figure 2:** Separation of a liquid and a solid, illustrating the meaning of the work of adhesion,  $W_{adh}$ , as the change in total free energy of the system when a solid/liquid interface is replaced by a liquid/air and air/solid interfaces.

Combination of Eqs. 8 and 9 gives the following:

$$W_{adh} = \gamma_{\ell} (1 + \cos \theta_e) \quad (10)$$

Equation 10 indicates that we can know the quantitative interaction between the liquid and the solid if we are able to measure the liquid surface energy,  $\gamma_{\ell}$  and the equilibrium contact angle,  $\theta_e$ . This purpose of this lab is to measure both of these quantities in some model systems and to show how these quantities can be easily modified. Before we do that, we need to talk about two important issues:

- The actual contact angle you will measure is almost certainly not going to be the equilibrium contact angle.
- Liquid surface energies are often measured by understanding the effect of gravity on a relatively small drop.

**Non-equilibrium effects:** In reality, the situation is more complicated than is implied by Eq. 8, and the contact angles you will measure depend on a whole bunch of factors, in addition to the surface and interfacial energies. Factors like surface roughness and surface inhomogeneities on the nanometer scale cause the measured contact angles differ from the  $\theta_e$ , and to depend on the details of the way the experiment is done. When a droplet is originally applied to the materials surface and the droplet volume is increasing with time, the contact angle is referred to an advancing contact angle,  $\theta_a$ . The receding contact angle,  $\theta_r$ , corresponds to the opposite situation, where the droplet size is shrinking. The advancing contact angle is larger than  $\theta_e$  and the receding contact angle will be less than  $\theta_e$ :

$$\theta_r < \theta_e < \theta_a \quad (11)$$

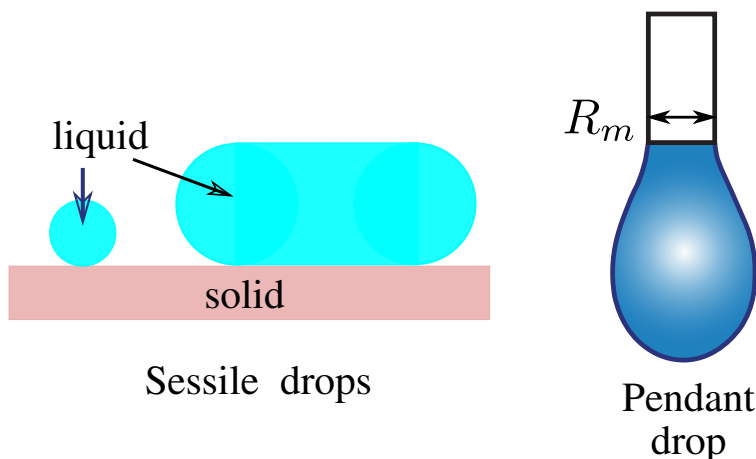
Generally you'll want to report both advancing and receding angles in your work. The difference between  $\theta_a$  and  $\theta_r$  is an important parameter referred to as the contact angle hysteresis, and controls the tendency of droplets to stick to an inclined surface.

**The Effect of Gravity and the Measurement of  $\gamma_{\ell}$ :** We know from experience that Eq. 7 can't work for very large droplets. Eventually, gravity flattens the droplet and the drop height,  $h$ , no longer continues to increase as  $r$  gets larger and larger. This situation is as shown in the left part



of Figure 3, where we show the behavior of small and large droplets sitting on a surface (sessile drops). The obvious question to ask here is ‘how small is small?’ and what controls the maximum value of  $h$  that can be obtained? The answer to this question is the capillary length,  $\lambda_c$ , which can be viewed as the radius of the spherical droplet for which the Laplace pressure inside the drop ( $2\gamma/R$ ) is equal to the gravitational hydrostatic pressure at the bottom of the drop ( $2\rho gR$ , where  $g$  is the gravitational acceleration and  $\rho$  is the liquid density). These pressures are equal to one another for  $R = \lambda_c$ , where  $\lambda_c$  is given by the following:

$$\lambda_c = \sqrt{\gamma/\delta\rho g} \quad (12)$$



**Figure 3:** ‘Small’ and ‘Large’ sessile drops (left) and a pendant drop (right) used for the quantitative determination of the liquid surface energy.

The capillary length determines the degree to which gravity distorts the droplet from a spherical cap, with no noticeable distortion observed for  $R \ll \lambda_c$ . The measurement can be done with sessile drops like those in the left part of Figure 3, but it is generally more accurately done for the pendant drop geometry at the right of Figure 3. The pendant drop geometry is used in this laboratory. The software automatically measures the shape of the droplet and determines the capillary length from the shape, which is then converted to a surface energy using Eq. 3 and a known value of the liquid density. (Note that the experiment can also be used to measure the interfacial free energy between two immiscible liquids, in which case  $\rho$  is replaced with the density difference between the liquids).

A reasonable estimate of the surface free energy can be obtained by continuously injecting liquid through the syringe needle with the pendant drop geometry and measuring the critical droplet volume,  $V_c$ , where a droplet detaches and a new one is formed. Droplet detachment happens when the force corresponding to the surface tension around the perimeter of the droplet ( $2\pi R_m \gamma_\ell$ , where  $R_m$  is the inner radius of the capillary) is equal to the gravitational force exerted by the droplet ( $\rho g V_c$ ). By equating these two forces we get the following approximate expression for  $\gamma_\ell$ :

$$\gamma_\ell \approx \frac{\rho g V_c}{2\pi R_m} \quad (13)$$

If you are interested in a more complete treatment of the entire problem, take a look at the first few pages of reference [3].

## Samples

The following materials will be provided:

- Clean water
- A soap solution that can be added to the water to reduce its surface energy
- A variety of materials expected to have different contact angles with water
- Access to a UV-ozone cleaner for surface modification

## Laboratory Procedure and Write-up

- First of all, answer the following questions and include a brief discussion the following points in your lab report:
  1. Look up the surface energy of pure water and write down the value of this quantity.
  2. Draw the shape of a sessile drop for  $\theta = 90^\circ$  and for  $\theta = 180^\circ$ , and show that Eq. 7 is correct in these two limits.
  3. What is the capillary length for water? Is this consistent with your own experience with how water behaves? Give a couple examples.
- Measure the interfacial tension of pure water and of a soap solution, using the full drop shape analysis.
- Measure the interfacial tension for one of the solutions from the previous experiment using the critical volume method, comparing the result you get with drop shape analysis with the value you get from Eq. 13
- Measure the advancing and receding contact angles for at least 5 solid surfaces, making an attempt to obtain the following:
  1. What surface/liquid combination gives the maximum value of  $\theta_a$ ?
  2. What surface/liquid combination gives the minimum value of  $\theta_a$ ?
  3. What surface/liquid combination gives the minimum contact angle hysteresis, expressed as  $\cos \theta_r - \cos \theta_a$ ?

In your writeup, describe potential applications where each of these surfaces would be useful.

- In your your writeup, describe the experimental protocol for measuring the surface tension and contact angles in sufficient detail so that the experiments could be repeated by other students, just by reading your procedures.

## References

- [1] H. Nakajima, [The discovery and acceptance of the Kirkendall Effect: The result of a short research career](#), JOM 49 (6) (1997) 15–19. doi:10.1007/BF02914706.
- [2] E04 Committee, [Test Methods for Determining Average Grain Size](#), Tech. rep., ASTM International (2013).  
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- [3] D. Carvajal, E. J. Laprade, K. J. Henderson, K. R. Shull, [Mechanics of pendant drops and axisymmetric membranes](#), Soft Matter 7 (2011) 10508. doi:10.1039/c1sm05703k.