Lab 3
Diffusion during Sintering of Cu Wire
27-202
Fall 2000

Objective

The objective of this experiment is to study the reduction in the surface area in an array of copper wires that result from high temperature annealing. The annealing temperature will have to be high enough for mass transfer to occur by diffusion.

Introduction and Background

Capillary driven processes (those processes that reduce the total interfacial energy) lead to densification and grain growth in granular systems. This laboratory exercise is intended to provide a concrete demonstration of a capillary driven process (sintering) that occurs in the solid state. The experiment is a recreation of the model sintering experiment originally conducted by Alexander and Balluffi. The original account of their work can be found in: B.H. Alexander and R.W. Balluffi, "The Mechanism of Sintering in Copper" Acta Met. 5 [10] (1957) 666-677.

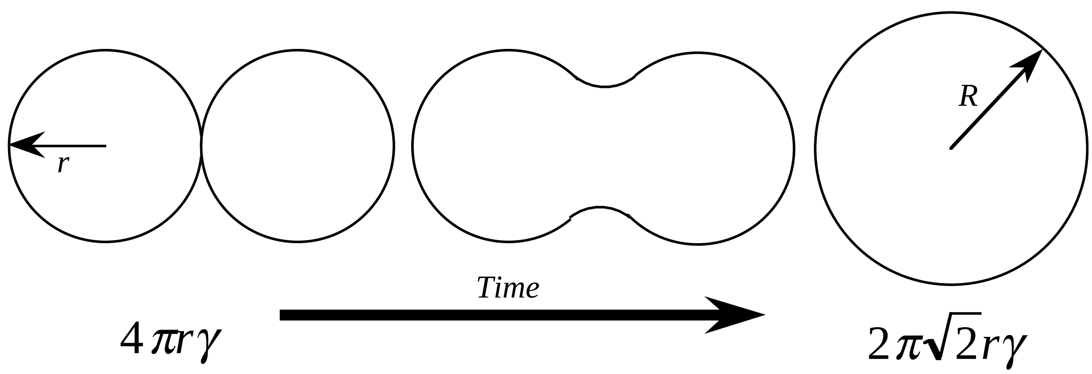

Figure 1. Schematic representation of surface energy driven shape changes.

Consider two copper rods, each of radius *r*, touching at a temperature such that diffusion is reasonably rapid (see Fig. 1). The total free energy of the system can be characterized by the volume free energy of each rod, ΔG_v, and the surface free energy of each rod, γ. Per unit length of rod, the total free energy of the pair of rods is:

$$G = 2(\pi r^2 \Delta G_v + 2\pi r\gamma)$$

If the two rods were to be combined into one rod of cross section $2\pi R^2$ (it can be shown by volume conservation that the new radius is R = $\sqrt{2}\,r$), then the free energy of the system will be reduced since $2\pi R\,\gamma$ is less than $4\pi r\gamma$. This relatively small change is enough to drive the densification process at a measurable rate at high temperatures. It would take a very long time to drive the proposed geometrical change to reach completion, in part because the driving force is continually being reduced as the shape evolves.

However, we can use a modified version of this experiment to illustrate the principle and to show the basis for the important processing technique known as sintering. Consider a collection of identical rods arranged in a close-packed configuration. If we can eliminate the near-triangular voids, we can reduce the surface energy and hence the total free energy of the system. There are some important, but difficult, concepts in discussing the detailed mechanisms by which this occurs so we will substitute a simple rule which serves to illustrate the intermediate stages (and happens to be correct). This rule says that surfaces move toward their center of curvature. Thus, the triangle goes through the stages illustrated in Fig. 2 until the free space is eliminated and densification has resulted.

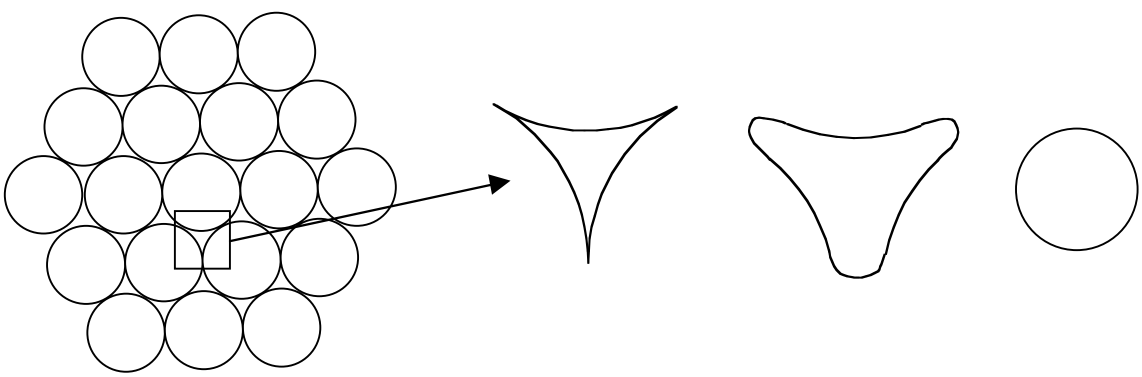

Figure 2. Shape evolution of the pores between the Cu wire. These shapes are schematic, and the volume decrease with time is not shown.

We can think of the free space between wires as being a collection of vacancies and the disappearance of this space as the result of these vacancies "dissolving" in the metal. Since at a given temperatures and pressures, only a very small number of vacancies is in equilibrium with the lattice, the extra defects must disappear permanently at "sinks". By far, the most effective sinks are large-angle grain boundaries where a vacancy can disappear in the poorly packed layers between the grains. Thus, we would expect the rate of sintering to depend on grain size (the mean distance to a sink).

We will study the reduction of surface area in an array of copper wires which are heated to a temperature sufficiently high that diffusion can cause mass transfer. The net result is densification and, for other reasons, grain growth in the copper (which may affect the rate of the reaction since it is largely these boundaries which consume the diffusing vacancies).

Equipment

1. A copper spool on which will be wound about six layers of 0.005" diameter pure copper wire so that each wire is in contact with six others (except for those on the surface).

2. A controlled atmosphere furnace for annealing the Cu spools. To prevent oxidation, you should flow H2 throughout the anneal. Non-explosive forming gas compositions (10% H2, balance N2) are adequate to prevent oxidation.

3. A vacuum pump and vacuum desicator.

4. A saw capable of cutting the spools in half, and standard metallographic polishing equipment.

5. An optical microscope, to observed the results.

Procedure

The samples should be annealed at 1000°C. The class should be divided up, so that each group can anneal their sample for a different time, between 8 and 80h. If there are N students in a group, then they should anneal N/2 spools. After putting the spools in the furnace, it should be thoroughly purged with the forming gas by evacuating and refilling at least three times. Next, establish a slow but continuous flow of the hydrogen containing gas and heat the furnace to 1000°C for the duration of the experiment.

After the annealing is complete, the spools should be embedded in a PMMA sample mount and cu tin half, parallel to the axis of the spool. To stabilize the pore structure for polishing, the samples should be surrounded by excesses PMMA, and put in a vacuum dessicator so that the polymer impregnates the pores before solidifying.

The samples can then be ground and polished to a mirror finish (be sure to grind through the region of damage created by the saw cut). Take optical micrographs of the unannealed and annealed specimens at an appropriate magnification to illustrate features you wish to discuss in your report. Make sure that you measure the field of view in the microscope, so that you can put scale bars on your images.

Report

Your report should be prepared in the sample format as the previous two and answer the following questions:

1. What is the original grain size of the copper wire? What is the grain size after annealing? How did you measure these grain sizes? What is the amount of scatter in your data?
2. How has the wire center-to-center distance changed after annealing? Report this figure along the axis of the spool and along the radius of the spool. How do you explain this?
3. What is your estimate of the change in surface energy per cm^3 of Cu after annealing of the specimen? The surface energy of copper is about 1 J/m^2. How does this compare with the change in grain boundary energy because of the grain growth? Take grain boundary energy as one half of the surface energy. Do these numbers bear any relation to each other? If so, why? If not, why not?
4. Calculate the void fraction in the sample and the "rugiosity" (the perimeter of the void divided by the circumference of a circle of equal area). What are the initial and final possible values of rugiosity?
5. Try to find and illustrate areas in your sample where void disappearance is more rapid than the average. Discuss why this occurs.