KINETICS OF GRAIN GROWTH

Introduction

In the previous two experiments hardness measurements were used to monitor the development of the microstructure, particularly the phases present and the relative amounts present, following prescribed heat treatments. Indeed, individual phases, their properties and their distribution in the microstructure have a significant effect on properties. Metallography can tell us about how the phases formed, how they are distributed in the microstructure, etc. Hardness testing and microhardness testing can measure the properties of the composite microstructure and each phase, respectively. After the types and morphology of the phase present, grain size is an obvious and important microstructural characteristics which has a significant effect on properties is the grain size. Grain size determines the mean distance between and the total volume occupied by grain boundaries and these grain boundaries can effect properties such as strength and ductility in a variety of ways.

As a purely structural defect, that is as a high angle boundary, grain boundaries can act as obstacles to slip as demonstrated in the Hall-Petch relationship. On the other hand, grain boundaries have a relatively "open" structure, so diffusion along the grain boundary is faster than in the lattice, thus the grain size dependence of Coble creep (where vacancies diffuse along the grain boundary instead of through the lattice), the lower activation energy of grain boundary diffusion and the grain size dependence of Nabarro-Herring creep (Grain size determines the distance between vacancy sources and sinks, i.e., grain boundaries, while diffusion is through the lattice.) To generalize a bit regarding the influence of grain size on the mechanical properties of materials, decreasing the grain size increases the strength at low temperatures while it decreases the strength at high temperatures.

From a thermodynamic standpoint, grain boundaries increase the total energy of a material. Therefore there is a tendency to reduce the total amount of grain boundary area and since large grains have less grain boundary area per unit volume than small grains then grain growth can achieve a reduction in the energy associated with grain boundaries. Also, it is well known that impurities segregate to the grain boundaries and this can lead to grain boundary embrittlement, ie. sulphur in steels and nickel based alloys. Finally, because grain boundaries are local regions of relatively high energy, they often act as nucleation sites for phase transformations. For example, martensite nucleates at grain boundaries and very quickly grows to form platelets that traverse the grain until they encounter a barrier such as the opposite grain boundary. Consequently, grain size effects the hardenability of steel.

Given the importance of grain size on so many aspects of a materials behavior it is important to understand the mechanism of grain growth and to be able to predict and even control grain growth rates. Over the years many studies have been made on recrystallization and grain growth. From these studies a number of rules about grain growth have been formulated. These rules, as listed by Burke and Turnbull [1] are:

1. Grain growth occurs by grain boundary migration and not by the coalescence of neighboring grains as do water droplets.

2. Grain boundary migration is discontinuous or jerky and its direction may suddenly change.

3. One grain may grow into a neighboring grain on one side while it is being consumed from another side.

4. The rate of consumption of a grain frequently becomes more rapid as the grain is about to disappear.

5. A curved grain boundary usually migrates towards its center of curvature.

6. When grain boundaries in a single phase meet at angles other than 120 degrees, the grain included by the more acute angle will be consumed so that the angles approach 120 degrees.

These rules have been the basis, and the demise, of a number of theories that attempt to describe grain growth in terms of more fundamental characteristics such as driving forces and mechanisms of grain boundary migration.

Grain growth can occur in any polycrystalline material but the full glory of the phenomenon is best revealed during and after the recrystallization of a cold worked material. Recrystallization is a process whereby the severely distorted (distorted by mechanical means) crystalline structure is restored to a "strain free" state. The driving force for recrystallization is the stored energy from the cold working, primarily due to the high density of dislocations. A mild anneal might be capable of decreasing the dislocation density somewhat, a process called recovery, but a more thorough anneal (higher temperature, longer time) can cause the original distorted grains to be replaced by a set of new strain free grains. Initially, these newly formed grains are quite small, having nucleated at sites where the local strain energies were greatest. However, once formed they can grow and the growth phase can be one of two types, normal or abnormal. Normal grain growth is characterized by a distribution of grain sizes does not change with time. But in highly textured materials abnormal grain growth, or secondary recrystallization, can occur. During secondary recrystallization a few grains grow at a high rate, consuming its neighbors, and often leading to undesirable mechanical properties.

Ideal grain growth is a special case of normal grain growth. In this case growth is driven only by the reduction of the total amount of grain boundary surface energy. Contributions of elastic strains, chemical and temperature gradients, etc. are neglected. Assuming that the rate of growth is proportional to the driving force and that the driving force is proportional to the total amount of grain boundary energy, then it can be shown that

$$d^2 - d_0^2 = k'\gamma t \qquad \textbf{(1)}$$

where d is the grain size, d_o is the initial grain size, t is time and γ is the grain boundary energy term. Since γ is independent of grain size the above equation can be simplified to

$$d^2 - d_0^2 = kt \qquad \textbf{(2)}$$

and if d_o is much smaller than d, then this can be simplified further to

$$d^2 = kt. \quad (3)$$

The term k is sensitive to temperature and is usually written as

$$k = k_0 \exp\left(\frac{-Q}{RT}\right). \quad (4)$$

The grain size as a function of time can also be expressed as

$$d = Kt^{½} \quad (5)$$

which is often rewritten as

$$\ln(d) = \ln(K) + ½\ln(t) \quad (6)$$

before analysis by graphical or numeric methods.

While theoretically the activation energy Q for grain boundary mobility should be equal to that for diffusion values which vary from 0.3 to 2.5 times that for diffusion have been reported. Also, the $t^{½}$ dependence is not always observed. Normally, lower values are observed. Nevertheless, ideal grain growth has been observed in ultra-pure metals at temperatures near the melting point. But even minor amounts of impurities can decrease the rate of boundary migration significantly (by a factor of 10^{11} for 0.01 w% Mn in Al) and increase the activation energy somewhat. Also, contributions to the total driving force can come from several other sources; surface energy, elastic energy, stored energy of deformation, magnetic fields, and temperature and composition gradients. Obviously while much is known about the nature of the driving forces for normal grain growth, the factors which determine grain boundary mobility are not.

In this experiment the grain growth behavior of the C26000 alloy is investigated. The annealing treatments are conducted at temperatures between 400°C and 750°C (it is expected to recrystallize at approximately 350°C) for from 1 to 100 hours. Grain sizes are measured using the mean lineal intercept method. Grain growth is assumed to obey a power law equation while the temperature dependence is expected to obey an Arrhenius relationship. Both the activation energy and growth exponent are measured. The grain growth behavior is compared to that for ideal grain growth.

Preparation

Before attempting this experiment one should be familiar with the certain technological and theoretical aspects of the experiment. One should also start thinking about possible outcomes of the experiment. The following questions should help get you started.

1. Non-heat treatable brasses like cartridge brass are sold in different conditions which designate the amount of cold work it has received. What is the typical hardness and approximate equivalent tensile elongation for 70/30 brass in the following conditions?

   a. Fully annealed
   b. Half hard
   c. Full hard
   d. Extra hard

2. Why is prior cold working important in this experiment? What effect would using either a softer or harder 70/30 brass have on this experiment?

3. Why should we bother to measure the hardness after each anneal when we are not interested in the mechanical properties?

4. What is the solidus temperature for this brass? What is the highest annealing temperature that we should use in this experiment? What is the lowest? Do we need to use a protective atmosphere during the heat treatments? Will this brass oxidize or dezinctify during the anneals? Should we support our specimens to prevent sagging during the anneals? After the annealing treatment, how should the specimens be cooled?

5. What is tracer diffusivity, trace self-diffusion and tracer impurity-diffusivity? How is tracer diffusivity relate to chemical interdiffusivity? Why would these be important in this experiment?

6. What is the activation energy for the tracer self-diffusivity of Cu? Zn? What is the diffusivity of Cu in Zn? Zn in Cu? Which is most relevant in this experiment?

7. Assuming power law grain growth behavior, compute and plot grain size versus time at the temperatures used in this experiment. Use values for K', Q and the exponent that you feel are appropriate. Plot the 650°C data again to measure the activation energy and exponent.

8. How do the annealing twins found in this material form?

9. Measure the grain size in the micrograph in figure 1.

10. Derive the relationship between the grain boundary area to volume ratio as a function of grain diameter.

Safety Considerations

This experiment involves heat treating brass, hardness testing the specimens and mounting and polishing them for metallographic observation. Extreme care should be exercised during the heat treating phase of the experiment as the temperatures can be quite high (800°C) and therefore poses severe burn hazards to personnel and fire hazards to the building. Slight hazards are associated with polishing and grinding the specimens. Novices invariably end up having a specimen or two snag the polishing cloth, sending their specimen flying across the room. The etchant which is used, ferric chloride plus hydrochloric acid, is not particularly aggressive but should be respected. The mounting presses are fully automatic and if the proper procedure is followed should pose not hazard to the students or the equipment. Operating instructions for the presses are kept nearby.

Chemical Hazards

Moderate. Etchants containing hydrochloric acid and ferric chloride are used. Appropriate personal protective equipment should be worn and the etchants should only be used in a safe out-of-the-way part of the laboratory which is set up for only etching the samples. Proper technique should be used for etching the specimens, washing the specimens and disposing of the etchant. MSDS's for each of the etchants or the components of each etchant are available. MSDS's are also available

for the polishing and grinding materials.

Physical Hazards

The potential for very serious burns exists. Temperatures approaching 800°C are used during these experiments. At these temperatures one can easily be burned while loading and unloading specimens from the furnaces, even if the hot specimens and furnace are not touched. It will be important to wear heat resistant gloves and to use long tongs. One should also take care to prepare a clear area to work, have an emergency procedure in place in case hot specimens are dropped on the floor, etc. It would be a good idea to rehearse the procedures for handling hot specimens.

Hardness testing poses very little hazard if proper testing procedures are followed. Using the proper anvil and indentor and a clean specimen will minimize the chance of damaging the equipment or injuring personnel.

The polishing wheels can spin at several hundred rpm. Take care during the grinding and polishing phases of the experiment that your fingers or the specimen do not get trapped between the spinning wheel and the bowl. Also, take a moment to bevel both the tops and bottoms of the specimens to remove sharp edges that might snag the polishing cloth or grinding paper, get ripped out of your hand, cutting your fingers and sending the specimen flying across the room.

The mounting presses are fully automatic. Simply follow the established procedures and there should be no problem.

Bio-hazards

None.

Radiation Hazards

None.

Protective Equipment

Recommended: safety glasses are recommended during the polishing/grinding and hardness testing phases of the experiment. The use of protective coverings for the floor and counter tops is also recommended.

Required: safety glasses, heat resistant gloves and long tongs for the heat treatment phases of the experiment. Safety glasses and chemical resistant gloves must be used when etching the specimens.

Waste

Pour used etchant back into the original bottle. The dilute ferric chloride etchant which was washed from the specimen can be poured down the drain. Other disposal procedures may be required if etchants other than ferric chloride are used.

Used specimens can be recycled as scrap copper/brass.

Materials

The alloy being studied is formally known as the C26000 alloy. It is also known as C260 (or simply 260), alpha brass, 70/30 and cartridge brass. It has many uses in architectural, electrical, hardware, munitions and plumbing industries. C26000 has a nominal composition of 70 w% copper and 30 w% zinc. It is a single phase alloy (alpha, bcc) up to its solidus at 915°C (check the Cu-Zn equilibrium phase diagram).

Specimens have been sheared from a ⅛" thick sheet of C26000 which was supplied in the half-hard condition. Specimens measure approximately ½" square.

Procedure

1. Preliminary

Measure the hardness of several specimens prior to annealing. Save one specimen for metallography. For the remainder, devise a simple numbering system to identify the specimens and engrave each specimen accordingly.

Table 1. Record of annealing procedures in the effect of temperature on grain size test.

Annealing Schedule			Actual Annealing Schedule			Actual Annealing Time
Annealing Temperature	Start Date	Start Time	Annealing Temperature	End Date	End Time	
450°C						
500°C						
550°C						
600°C						
650°C						
700°C						
750°C						

2. Effect of Temperature

Set the furnaces at the temperatures listed in table 1. Anneal one specimen at each of these temperatures for the agreed upon length of time (1 or 2 hours). Other temperatures and times may also be used but you must take steps to ensure that the material has fully recrystallized, a concern at lower annealing temperatures and times, or does not oxidize excessively (higher temperatures and longer times). Hardness test each specimen after the anneal.

Table 2. Hardness of C26000 following 2 hour anneals at different temperatures.

Annealing Temperature	Rockwell Hardness, HRF					
	Hardness Reading 1	Hardness Reading 2	Hardness Reading 3	Hardness Reading 4	Hardness Reading 5	Average Hardness
450°C						
500°C						
550°C						
600°C						
650°C						
700°C						
750°C						

3. Effect of Time

Anneal specimens at the agreed upon temperature for 1, 2, 5, 20, 50, 100 hours and longer if you wish. Air cool when done. (Other temperatures and times may be used.) Hardness test each specimen after the anneal.

Table 3. Record of annealing procedures the effect of time on grain size test.

Annealing Schedule			Actual Annealing Schedule			Actual Annealing Time
Annealing Time	Start Date	Start Time	Annealing Time	End Date	End Time	
1 hour						
2						
4						
10						
20						
24						
50						
100						

Table 4. Hardness of C26000 as a function of annealing time.

Annealing Time	Rockwell Hardness, HRF					
	Hardness Reading 1	**Hardness Reading 2**	**Hardness Reading 3**	**Hardness Reading 4**	**Hardness Reading 5**	**Average Hardness**
1 hour						
2						
4						
10						
20						
24						
50						
100						

4. Metallography

Specimen preparation involves producing a planar section of a material that reveals its true microstructure. Specimen preparation must be done carefully so as not to alter the microstructure in any way. The sectioning and grinding procedures produce a damaged layer near the surface, but careful grinding will minimize this damage while polishing will gently remove the last of the damaged material. The surface can then be etched to reveal grain boundaries, particles, twin boundaries, inclusions, etc.

The basic procedure to use in this experiment follows:

- Mount the specimen in a suitable medium (Transoptic powder, Bakelite, etc.)
- Wet grind in four steps using 240, 320, 400, then 600 grit SiC. Be careful the keep the specimen flat, to not bevel it. Rinse the specimen between grinding steps and clean the specimen thoroughly before proceeding to the next step.
- Rough polish using 6 micron diamond paste on a nylon polishing cloth. Don't use water on this cloth. Use small amounts of the oil-based extender. Clean the specimen thoroughly before proceeding to the next step.
- Final polish using 0.05 micron Al_2O_3 and distilled water on Microcloth or a similar flocked cloth. Clean the specimen thoroughly before proceeding to the next step.
- If necessary an additional final polish will be done using a vibratory polisher. Often this is the only way to get good results on materials such as brass.
- Etch in an alcohol-HCl-$FeCl_3$ solution to reveal the microstructure. Be very careful to not over-etch or you may have go back to the final grinding (600 grit) step.

5. Measuring Grain Size

The lineal intercept method (ASTM E-112, sections 9, 10 and 12) is considered to be the most efficient method for measuring the mean grain size. It is widely used in research and in industry as a quality control procedure. It can be used to measure the grain size of single and multi-phase materials and equiaxed or aligned microstructure. Look up the ASTM E112 standard and read through it. Refer to the appendix for a step-by-step description of the procedure.

Table 5. Grain sizes after annealing at different temperatures but for the same length of time. Statistics are given for a 95% confidence level.

Annealing Temperature	Number of Samples	Mean Number of Intercepts	Standard Error	Mean Intercept Length	Confidence Interval
450°C					
500°C					
550°C					
600°C					
650°C					
700°C					
750°C					

Table 6. Grain size of C26000 as a function of annealing time for anneals conducted at 650°C. Statistics are given for a 95% confidence level.

Annealing Time	Number of Samples	Mean Number of Intercepts	Standard Error	Mean Intercept Length	Confidence Interval
1 hour					
2					
5					
10					
20					
24					
50					
100					

Analysis

The following questions should help you analyze the results and to begin to develop the ideas you will put into your report.

1. Do any of the hardness measurements indicate that we might not have produced a fully recrystallized microstructure in any of the anneals?

2. Does the grain size data show a steady trend with respect to annealing temperature and time? If not, why? Compare the grain sizes obtained by our anneals with published data for a similar material and anneals.

3. Determine the activation energy using the data obtained from table 3. How does it compare with the activation energy for tracer self diffusivity of Cu or Zn in Cu? How does it compare with the activation energy for grain growth from the data in figure 1?

4. Plot the grain size -vs- time data in a manner that allows you to measure the grain growth exponent. Was ideal grain growth observed? If not, can you suggest a reason why the grain growth behavior was not ideal?

5. Plot the experimentally obtained data and the equation for grain growth using the activation energy and growth exponent determined in this experiment. Do they agree?

References and Further Reading

1. J.E.Burke and D.Turnbull, Progress in Metal Physics, v.IIIB, p.220, (1952).

2. Properties and Selection: Nonferrous Alloys and Pure Metals, Metals Handbook, ninth edition, ASM International, Metals Park, OH, volume 2., (1979). (UCD PSL: TA 459 A5 1978 v2 (REF))

3. Heat Treating, Metals Handbook, ninth edition, ASM International, Metals Park, OH, volume 4, (1981). (UCD PSL: TA 459 A5 1981 v4 (REF))

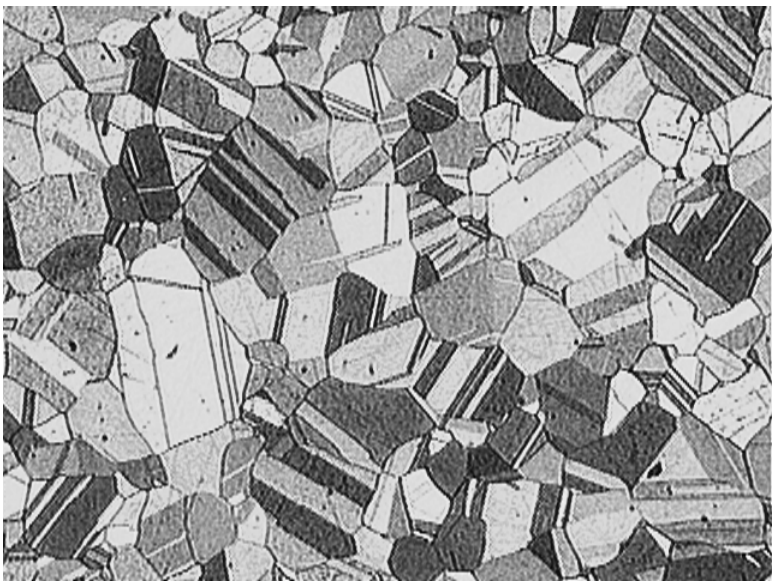

Figure 1. Microstructure of full-hard 70/30 brass after being annealed at 575°C for 1 hour. Magnification: 143X.