# *Spreadsheet Applications for Materials Science*

## *Grain Growth Kinetics of the C26000 Alloy*

### Introduction

The C26000 alloy 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 (α, bcc) up to its solidus at 915°C.

Because C26000 is a single phase alloy it is not considered heat treatable, but it can be strengthened by cold working and softened by annealing. The high work hardening rate of this alloy means cold working can increase the yield strength dramatically, from 75 MPa in the fully annealed condition to over 450 MPa in the full-hard condition. Along with this increase in strength comes a decrease in ductility, from 68% down to 5%. Recovery annealing will restore a small amount of ductility with little change in strength and hardness. Annealing that results in recrystallization can extend the ductility considerably and can more than halve the hardness and strength. Further annealing will lead to grain growth which can produce further decreases in strength and increases in ductility, but can also lead to a lower fracture toughness and, if grain size is too large, to an undesirable orange peal surface following subsequent forming.

C26000, a single-phase alloy, offers an opportunity to study the grain growth behavior of a relatively simple material that is also widely used in industry. Modeling using spreadsheets and the analysis of data from experiments will be used to see if ideal grain growth behavior is observed in this alloy.

### Grain Growth Kinetics

Essentially, grain growth involves atoms from one grain crossing the boundary to join the adjacent grain. As a result the first grain becomes smaller and the second grain larger. There may be a number of factors driving this process, including the reduction in grain boundary surface area, strain,

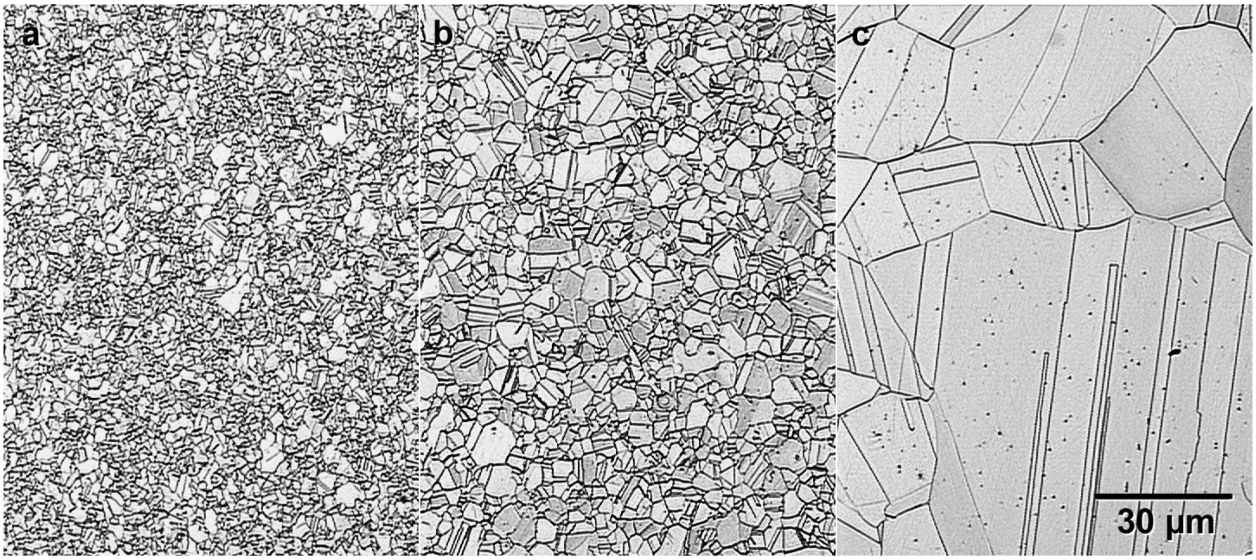

**Figure 1** Microstructure of C26000 alloy after annealing: a) 1 hour at 450°C, b) 1 hour at 550°C, c) 2 hours at 750°C.

curvature of the boundaries, magnetic fields, and chemical potential gradients. Boundary migration can be slow and steady but it has also been known to be very sudden, where one boundary can quickly sweep across a neighboring grain. Over the years many studies of recrystallization and grain growth have been made. From these studies a number of rules about grain growth have been formulated. These rules, as listed by Burke and Turnbull [1] are:

- Grain growth occurs by grain boundary migration and not by the coalescence of neighboring grains as do water droplets.
- Grain boundary migration is discontinuous or jerky and its direction may suddenly change.
- One grain may grow into a neighboring grain on one side while it is being consumed from another side.
- The rate of consumption of a grain frequently becomes more rapid as the grain is about to disappear.
- A curved grain boundary usually migrates towards its center of curvature.
- 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.

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

$$d^n - d_0^n = K\gamma t \qquad \textbf{(1)}$$

where $d$ is the grain size, $d_o$ is the initial grain size, $t$ is time and $\gamma$ is the grain boundary energy term and $n$ is the grain growth exponent which is equal to 2 for the case of ideal grain growth. Since $\gamma$ is independent of grain size the above equation can be simplified to

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

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

$$d^n = kt. \qquad \textbf{(3)}$$

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

$$k = k_G D \qquad \textbf{(4)}$$

where $D$ is the diffusivity. In ideal grain growth the activation energy $Q$ for grain boundary mobility is equal to that for diffusion. Values which vary from 0.3 to 2.5 times that for diffusion, however, have been reported. Also, the ideal $t^{1/2}$ dependence is not always observed. Normally, lower values are observed. Minor amounts of impurities can decrease the rate of boundary migration significantly 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. Nevertheless, ideal grain growth has been observed in ultra-pure metals at temperatures near the melting point.

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## Spreadsheet Exercises

The following exercises will take you from some preliminary issues related to grain growth through the analysis of actual data from experiments performed on the C26000 alloy. They start with a look at the diffusivity of Cu, Zn and Cu-Zn alloys, followed by modeling the ideal grain growth for this alloy. The results from the modeling are then analyzed as if they were experimental results, providing an opportunity to develop and test your analysis procedure. Finally, grain growth data from actual annealing treatments are analyzed.

### *1. Diffusivity in the Cu-Zn system*

In this exercise you will look at the diffusivities that are relevant to the study of grain growth of the C26000 alloy. The appendix lists the diffusivities from a number of studies of Cu, Zn and Cu-Zn alloys. Use this information to do the following:

- Calculate the diffusion rate at 500°C and the diffusion rate relative to the first entry in the appendix. Plot the log of the diffusivity for each solute/solvent combination using a bar chart. Experiment with different temperatures to see how the results change.

- Calculate the diffusivities for temperatures from 400°C (slightly above the typical recrystallization temperature) to 800°C (below the solidus). Plot the log of the diffusivity as a function of the versus inverse temperature.

Note the typical and range of values you get in the first set of calculations. From these results what can you say about the diffusivity of copper, zinc and copper/zinc alloys?

Review the plot generated in the second set of calculations. Do the slopes, which are proportional to the activation energies, vary significantly? Which solute/solvent pairs do you find near the top of the plot, near the bottom, and in the middle?

Write a brief 1-2 page summary of what you learned about the diffusivity of copper, zinc and copper/zinc alloys and the relevance to this study of the grain growth of the C26000 alloy. Copy/paste your plots into this report. Include a printout of your spreadsheet, scaled to fit on one or two pages.

### *2. Modeling ideal grain growth of the C26000 alloy*

In this exercise you will use the above equations to build a simple computer model for the ideal grain growth of the C26000 alloy and to analyze the data as if it had come from an actual experiment. Use this model to do the following:

- Calculate the grain size for heat treatments conducted at 400, 500, 600, 700 and 800°C and for times ranging from 0 to 12 hours in steps of 0.5 hours. Adjust the value of $k_G$ so that grain sizes up to a centimeter (quite large) can be obtained for the 12 hour, 800°C heat treatment. Also, experiment with the value of $n$ and with the diffusivity.

- Plot the results in a standard xy plot that uses linear scaling for both the x and y axes.

- Plot the log of the grain size versus the log of the annealing time for all temperatures. Determine the value of $n$ and the intercept from this plot.

- Plot the log of the grain size versus the inverse temperature for annealing times of 1, 2, 5 and 10 hours. Determine the value of $Q$ and the intercept from this plot.

- Optionally, plot $\log(d^n/t)$ versus the inverse temperature for all annealing times. Again, determine the value of $Q$ and the intercept from this plot.

- Compare the values of $n$, $Q$ and the intercepts obtained from your analysis to those used in the equation for ideal grain growth.

Write a brief 1-2 page summary of what you learned about ideal grain growth of the C26000 alloy and on your ability to analyze the data as if it came from an actual experiment. Copy/paste your plots into this report. Include a printout of your spreadsheet, scaled to fit on one or two pages.

### *3. Analysis of the grain growth kinetics of the C26000 alloy*

In this exercise you will analyze the results of an experiment performed by students in 1989. The alloy studied was supplied in the half-hard condition. Samples measuring ½" square were cut from ⅛" thick plate and annealed in air at the temperatures and times listed in table 1. (All annealing temperatures were above the recrystallization temperature.) They were then mounted, polished and etched using standard metallographic specimen preparation procedures. The microstructures were analyzed with the aid of optical microscopes and the grain sizes were measured using the mean-lineal intercept method. The grain sizes reported in table 1 are the equivalent grain diameters.

- Plot hardness as a function of grain size. Given the decrease in hardness from the as-received sample to the annealed samples, do you think the sample had recrystallized fully?

- Analyze the data in table 1 in terms of ideal grain growth. Create plots for each step in the analysis. Determine the values of $n$, $Q$, and $k_G D_0$.

- Using the values of $n$, $Q$, and $k_G D_0$ determined in this work, calculate the grain size and compare these to measured values by plotting measured -vs- calculated grain sizes.

Table 1. Hardness and grain size as a function of annealing times and temperatures.

| Temperature °C | Time hours | Hardness HRF | Grain Size µm |
|---|---|---|---|
| A.R. | n/a | 103 (81 HRB) | n/a |
| 426 | 1 | 76 | 15.5 [1] |
| 538 | 1 | 67 | 27.3 |
| 676 | 1 | 40 | 210 |
| 750 | 1 | 36 | - |
| 426 | 2 | 73 | 18.9 [1] |
| 538 | 2 | 68 | 24.3 |
| 676 | 2 | 38 | 163 |
| 750 | 2 | 32 | 660 |
| 550 | 1 | 67 | 27.7 |
| 550 | 2 | 68 | 24.2 |
| 550 | 2 | 66 | 31.7 |
| 550 | 5.5 | 57 | 46.4 |
| 550 | 10 | 55 | 56.8 |
| 550 | 22 | 54 | 91.8 |
| 550 | 50.25 | 56 | 116 |
| 550 | 173 | 50 | 114 |
| 550 | 500 | 30 | - |

Note 1 - Much smaller grain sizes were expected, and these measurements can be difficult to make. Also, the students doubted these specimens had fully recrystallized.

Write a brief 1-2 page summary of how you conducted your analysis and what the essential results were. Comment on the relationship between hardness and grain size. Is the activation energy close to any of those listed in the appendix? Was ideal grain growth observed? Explain your answers. Copy/paste your plots into this report. Include a printout of your spreadsheet, scaled to fit on one or two pages.

## 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).
3. Heat Treating, Metals Handbook, ninth edition, ASM International, Metals Park, OH, volume 4, (1981).

## Appendix. Diffusion Coefficient for Copper, Zinc and Copper-Zinc Alloys

| Solvent | Solute | Do, $cm^2/s$ | Q, J/mol | Do, $cm^2/s$ | Q, J/mol | Temperature Range, °C | Solidus Temperature, °C | Note |
|---|---|---|---|---|---|---|---|---|
| **Tracer Self-Diffusivity** | | | | | | | | |
| Cu | Cu | 0.1 | 196862 | 2 | 233565 | 300-1061 | 1083.4 | $Cu^{64}$, reference |
| Cu | Cu | 0.38 | 203642 | - | - | 300-1061 | 1083.4 | $Cu^{64}$ |
| Cu | Cu | 0.78 | 210924 | - | - | 698-1061 | 1083.4 | $Cu^{64}$ |
| Zn | Zn | 0.13 | 91651 | - | - | 240-418 | 419.6 | $Zn^{65}$ |
| Zn | Zn | 0.18 | 96255 | - | - | 240-418 | 419.6 | $Zn^{65}$ |
| **Tracer Impurity Diffusivity** | | | | | | | | |
| Cu | Zn | 0.34 | 190836 | - | - | 605-1049 | 1083.4 | $Zn^{65}$ |
| Cu | Zn | 0.73 | 198787 | - | - | 890-1075 | 1083.4 | $Zn^{65}$ |
| Zn | Cu | 2.22 | 123583 | - | - | 338-415 | 419.6 | $Cu^{64}$ |
| Zn | Cu | 2.0 | 125215 | - | - | 338-415 | 419.6 | $Cu^{64}$ |
| **Diffusivity in Homogeneous Alloys** | | | | | | | | |
| 69.8 Cu | 30.2 Zn | - | - | 0.32 | 164470 | 700-900 | ~915 | Diffusion of $Zn^{65}$ in Cu |
| 69 Cu | 31 Zn | 0.34 | 175351 | 0.73 | 170329 | 580-905 | ~915 | Diffusion of Zn in α-phase |
| **Chemical Diffusion Coefficients** | | | | | | | | |
| 72 Cu | 28 Zn | 0.016 | 124294 | - | - | 724-910 | ~915 | $D_{Cu}$ and $D_{Zn}$, α-phase |
| 72 Cu | 28 Zn | 2.1 | 172422 | - | - | 700-910 | ~915 | $D_{Zn}$ in the α-phase |
| 72 Cu | 28 Zn | 0.81 | 178699 | - | - | 700-910 | ~915 | $D_{Cu}$ in the α-phase |
| 72 Cu | 28 Zn | 1.7 | 172840 | - | - | 724-910 | ~915 | $D_{Cu}$ and $D_{Zn}$, α-phase |

References: Smithells Metals Reference, 6th edition, Eric Brandes, ed., Butterworths, London, chapter 13 (1983) and CRC Handbook of Chemistry and Physics, 65th edition, CRC Press, Inc., Boca Raton Florida, F-46 - F-53, (1984).