Practical 2P1

Diffusion

What you should learn from this practical

Science
The practical aims to familiarise you with a solution of Fick's Second Law of diffusion by studying the diffusion of carbon into iron. The treatment makes the simplifying assumption that the diffusion coefficient, D, for carbon in iron is independent of concentration for the case where surface concentration is maintained constant. The quantitative analysis of microstructures will show you how to determine D values from solute profiles, which can be compared with published and theoretical data.

Practical skills
You will gain experience in the use of image processing software for quantitative metallography. Heat treatment (pack carburisation) in furnaces, preparation of metallographic sections and etching will be demonstrated. Results will be processed using a spreadsheet for curve fitting; you will need to write the spreadsheet functions. The microscopy will require interpretation of some complex microstructures.

Safety
In the pack-carburisation demonstration, care is needed in handling hot crucibles. This must be done using proper tongs, and wearing suitable protection (gloves and visor). Hot materials must not be left on the bench without a notice that they are hot and the time they were placed there. Normal safety precautions are adequate for the etches used here, i.e. lab coat, gloves and eye protection.
Overview of the Practical

1. The pack-carburisation of a sample of Swedish Iron (ferrite with a very low carbon content) will be demonstrated. This is an industrial process used for case hardening. At the temperatures used, carbon is diffusing in single-phase austenite. Metallographic sections have been prepared.

2. You will record digital images of the structures from different diffusion conditions so that quantitative measurements of phase areas/volumes different depths can be made using basic image analysis software.

3. You will determine carbon profiles by measuring the proportions of the constituents (e.g. primary ferrite, pearlite and primary cementite) in the normalised structures at selected depths and then calculating the mean carbon content for each depth.

4. Different ways will be used, and compared, to determine D from the error function solution of Fick’s Second Law. The results at two temperatures are combined to give the approximate activation energy.

5. You will need to plan the work so that all samples can be analysed in the time available.
Experimental details

Heat treatment

The samples are small pieces of Swedish Iron; this has a low C content and is almost entirely single-phase ferrite (some specimens may contain a small amount of pearlite).

The pack carburisation of these samples will be demonstrated:

- The samples are packed in a graphite / fireclay crucible in a mixture of powdered charcoal and sodium carbonate activator (10 % w/w). The carbonate releases carbon dioxide that reacts with the charcoal give carbon monoxide and forms a carburising gas. A lid is needed to exclude air, even while the crucible is cooling, or the surface will begin to decarburise.

- The crucible is placed in the furnace for 1 hour at a temperature in the region of 1000°C.

- At the end of the carburisation the crucible is allowed to cool in the furnace (switched off) to at least 500°C before removing from the furnace to cool more rapidly. This leaves some uncertainty in the time of treatment and give increased D values, but ensures equilibrium microstructures.

**Do not remove the lid until the crucible is completely cold. A suitable warning is must be placed while it is still hot**
Metallography

The heat treated samples have been cut in half transversely and mounted, then ground, polished and etched for examination. You may need to refresh the etched surfaces.

- After grinding, which needs to remove distorted metal from sawing during coarse grinding, and polishing, the specimens have been etched, in 2% nital. It is important that the samples have the best possible surface finish before etching, because the presence of scratch marks will interfere with the subsequent image analysis procedures.

- The etch time needs to be sufficient to show the structure clearly across the whole carbon profile, and a time of a few seconds should be ample. If the ferrite matrix has begun to etch (for example, along the lines of any residual scratch marks), then the sample is over-etched. In this case, the sample needs to have the final polish repeated and it needs to be etched with a shorter etching time.

- If the heat treatment has been carried out correctly your samples will have a 'case' of carburised iron of uniform depth around the whole circumference. The specimens have been cut to examine the mid-section metallographically, and not the end faces of the specimens. This is because carbon diffuses into the samples from the ends as well as from the sides. It is not possible to obtain a valid one-dimensional diffusion profile if the carbon is diffusing into area of interest from two different directions.
Recording and Image Analysis of Micrographs

Using correctly prepared specimens, you need to record images along a line perpendicular to the surface, and then analyse these to obtain the proportions of the microstructure constituents.

Instructions for image acquisition and analysis using the AxioVision software are given in Appendix A.

- In your images, select rectangles parallel to the surface at regular intervals and measure the proportions of each constituent by selecting the areas in each rectangle that are above a chosen threshold of intensity.

- You need to think carefully about the size and position of these rectangles, taking the observed microstructure into account.

In principle, the image analysis should be able to estimate the proportion of proeutectoid and eutectoid phases present for both the hypereutectoid and hypoeutectoid regions. However, proeutectoid cementite formed in hypereutectoid steels gives rise to difficulties in image processing. This cementite is mainly in the form of thin films at the prior austenite grain boundaries, and analysis by image thresholding cannot readily identify these.

The recommended procedure is to estimate the volume fraction of pearlite in the hypoeutectoid regions (i.e. from near zero carbon up to about 0.8 wt.% carbon), and not to attempt measurements in the hypereutectoid regions. Instead, you may assume that the carbon content at the outer edge of the sample corresponds to the saturation carbon content in austenite for the temperature at which the carburisation heat treatment was carried out. This value can be obtained
from the iron-carbon phase diagram, which can be found in any standard reference handbook.

Using the iron-carbon phase diagram, you then need to obtain data for the atomic \% carbon against depth. You will need to plan your work to see that everybody has the opportunity to contribute to this operation.

Advice on the calculations and data processing needed to obtain the carbon concentration profile is given in Appendix B.
Analysis of Results to obtain Carbon Diffusivity

If we make the assumption that diffusivity, D, can be treated as a constant (in reality there is some variation across so wide a range of concentration) and put constant surface concentration as a boundary condition, Fick's law can be solved to give:

\[ C(x,t) = C_s - (C_s - C_0) \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \]

You can analyse a Fickian concentration profile to obtain values of the diffusivity by three related methods:

1. A simple, but accurate, way to determine D is to find the depth (x) at which the carbon concentration is half that at the surface (neglecting the original low level in the iron, by assuming that \(C_0=0\)). The error function (\text{erf}) has a value very close to 0.5 at this point, and hence for this depth, \(x = \sqrt{Dt}\). Thus, knowing the value of x (and t), D may be calculated. You should check that the value for this depth increases linearly with the square root of diffusing time.

2. Another approximate way, if the surface concentration is uncertain, is to take the total case depth as roughly \(2\sqrt{Dt}\). You should check this also with your data, and consider whether the assumption that \(C_0=0\) is valid.

3. A better way is to use the full theoretical solution, and obtain a value of D for the best fit of this function to your data. This can be done using a spreadsheet. The sensitivity to variations in \(C_0\) can also be considered.
You should:

- Use the D values that you obtain by these different ways to test the expected result that the same value of diffusivity is obtained irrespective of the time of heating at a given temperature.

- Use the variation of D with temperature to determine an activation energy for carbon diffusion.

**Bibliography**

For a short discussion of carburising/diffusion see Porter and Easterling "Phase transformations in Metals and Alloys" pp 73:4; there is a succinct treatment of the relevant maths in J.W. Christian "The Theory of Transformations in Metals and Alloys" pp 385-387. You are recommended to review these.

Fuller treatments can be found in P.G. Shewmon "Diffusion in Solids" or J. Crank "The Mathematics of Diffusion".

The following (rather old, but still relevant) papers are worth reading, and are available online.


- The diffusivity of carbon in iron by the steady-state method, R. Smith, Acta Metallurgica, 1, 578 (1953)
Write up

The allocated marks will be moderated following the discussion of your report in the marking session

The required report is brief, and should contain a concise description (< 1 page) of the experiment method.

You must include a print out of a representative image of one sample, accompanied by sketches and explanations of the structure. There must be a graph (or graphs) reporting the carbon content/distance data from each of your samples and a table summarising the D values obtained by the different methods described above. You must compare the D values and activation energy that you obtain with values from the literature.

It is very important to explain and justify your analysis method, including the choices that you made in the image analysis and their effects on errors and uncertainties. You need to explain or demonstrate why the particular solution of Fick's Law used applies to the boundary conditions of your experiment.

This first part of the report carries 50% of the marks

At the end of your report, answer the following questions.

1. There is sometimes a light coloured layer at the free surface of some samples. What do you think it is? Explain your judgement.

2. Describe the physical significance of the value of activation energy for carbon diffusion.

3. Explain what the carbon profile should look like if carburising were carried out at 850ºC.
4. Comment on whether your data show that D increases or decreases with carbon content? What is the expected result from theory?

5. Describe briefly the analysis method by which the value of D for any carbon content can be obtained from an accurate carbon concentration curve.

*This second part of the report carries the remaining 50% of the marks.*
Appendix A: Image Analysis

1. Open AxioVision

Using the Standard Workflow:

2. Check AutoScaling is on – on the Measure Toolbar.

3. Select the same objective on the microscope and from the workflow (usually x10).

4. Open the Live image.

5. Open live properties: check that the camera is set to Black and White mode (via Frame tab) and adjust the camera to give a good exposure. (via Adjust tab).

6. Snap the image.

Using the Diffusion Workflow:

7. Define regions of interest using the ‘Aligned Rectangle’ Tool.

8. Select “Burn in annotations” from Annotations menu: this records the locations of your selected areas on the image. (Later you may, if you wish, use the image to check your measurements of ferrite and pearlite areas by the line-intercept method). Click “ok” at the window and do not click “apply”.

9. Record the locations of the rectangles from the µm scale bar at the top.

10. Save your image.

11. Using the select ROI tool to select each of your regions, in turn:
    a. Copy the ROI.
    b. Paste it into fresh image.
c. You can then move your ROI box to obtain more images of exactly the same size, and repeat steps (a) and (b).

12. Close the main image.

13. Click “Run Program” and check the options are:
   a. Image Acquisition – Open Images, Automatic on. (you can also manually click the images you want)
   b. Measurement Data – Append off. Set your results file name here.
   c. Scaling – Apply Scaling From the Image on.

14. Execute the measurement – this will run through the available images.

15. In the Segmentation dialogue:
   a. Ensure “Phases may overlap” is off (default).
   b. Check “Phase1” is selected and use the dropper to define the white phase. You can then define Phase 2 using the same method.
   c. Adjust the threshold for the best segmentation.
   d. Click continue for each image and obtain the result.

Alternatively

You can use alternative image analysis software on your own computer, if you would like to. For instance, ImageJ is free, open source software that is widely used for scientific image analysis, and it is possible to batch process images. It can be downloaded from http://imagej.net. However, you will need to teach yourself how to use it.
Appendix B: Data Analysis

Carbon Concentration Profiles

For the diffusion analysis, you need to calculate the atomic % of carbon as a function of distance from the sample edge, and hence obtain a carbon concentration profile.

This is done using the iron-iron carbide phase diagram, assuming equilibrium conditions. It is also assumed that the fraction of phases observed in your sample is the same that existed at the higher temperature at which it formed. Under equilibrium conditions, the eutectoid reaction occurs at 723°C. The eutectoid composition at this temperature is 0.8 wt% carbon, while the solubility of carbon in ferrite is 0.035 wt%. The carbon content of cementite (Fe₃C) is 6.67 wt%.

The image analysis will give you the total number of pixels in your selected analysis area, and the number of pixels above or below your chosen threshold. For instance, if the ferrite is light, this can be used to calculate the area fraction of ferrite. Assuming a binary microstructure, depending on whether you have a hypo or hypereutectoid composition, the area fractions of the other constituents such as pearlite or cementite can then be calculated.

Assuming the area fractions of the constituents A and B in a two-dimensional section are the same as the volume fractions in the microstructure, the weight fraction \( A_{\text{wt\%}} \) of constituent A with density \( \rho_A \) and volume fraction \( A_{\text{V\%}} \) is calculated as below.

\[
A_{\text{wt\%}} = \frac{A_{\text{V\%}} \rho_A}{A_{\text{V\%}} \rho_A + B_{\text{V\%}} \rho_B}
\]
It is essential that you read through all of this document before the laboratory class

The approximate densities of pearlite, ferrite and cementite are 7.5, 7.9 and 4.0 g/cm$^3$, respectively.

You can use the inverse lever rule and the phase diagram to then calculate the carbon weight concentration from the weight fractions, such as the ferrite and pearlite content.

Finally, the atomic concentration, $A_{\text{at}\%}$, is obtained from the weight concentrations using equation below, where $A_{\text{atom}}$ and $B_{\text{atom}}$ are the atomic weights of elements A and B. The atomic weights of iron and carbon are approximately 55.9 and 12.0 respectively.

$$A_{\text{at}\%} = \frac{A_{\text{wt}\%} B_{\text{atom}}}{A_{\text{wt}\%} B_{\text{atom}} + B_{\text{wt}\%} A_{\text{atom}}} \times 100$$

You will have a quite large number of calculations to do, particularly to make an assessment of the measurement uncertainty in your carbon concentration data, so you are advised to construct a spreadsheet using software such as Excel$^1$. However, you can use alternatives, such as Matlab, if you wish.

In Excel, it is suggested you record the position of each observation down a column of cells in the spreadsheet, with the raw data for the

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$^1$ If you are unsure how to use formulas in Excel, consult the “help” section “Creating Formulas”, particularly the section “Enter a formula that refers to values in other cells”.

Remember that to quickly apply a formula to the next cells down in the column, double-click the fill handle on the first cell that contains the formula. Excel calculates the results in each cell of the column automatically.
number of pixels in the image and thresholded selections in the next columns. You can then calculate the area fractions, weight fractions, area fractions etc. in further columns to the right.

**Diffusion and the Error Function**

A simple way to estimate the diffusion coefficient is to apply Fick’s law to predict the concentration profile and compare this to your data. Assume an initial value of the diffusion coefficient, D and then adjust this to get the best fit.

*Note: Take care with your units! The carbon diffusivity in iron at austenitisation temperatures is of the order of $10^{-11} \text{ m}^2 \text{s}^{-1}$.*

You can judge the fit by eye, but you should consider more quantitative ways of comparing the data and prediction. You should also consider the scatter (i.e. variability) in your data and the uncertainty in your measurements. You can then obtain a best estimate value of the diffusion coefficient and your confidence in it.

Fick’s Law is given

$$C(x,t) = C_s - (C_s - C_0) \text{erf}\left(\frac{x}{\sqrt{4Dt}}\right)$$

The Error Function, $\text{erf}$, is the indefinite integral defined by the equation

$$\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} dy$$
The function $\text{ERF}^2$ is used in Excel to calculate the Error Function, $erf$. For carburisation, the surface concentration ($C_s$) needs to be obtained from the phase diagram at the temperature of the carburisation. The bulk concentration, $C_0$, should be estimated from the bulk microstructure of your samples.

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$^2$ If you are unsure how to use this function, see the Help section in Excel under "ERF Function". Typing "=ERF(A1)" into a cell will calculate $erf(z)$ where $z$ is the value in cell A1.