

## **Practical 2P5**

### **Diffusion**

#### **What you should learn from this practical class:**

##### **Science**

The practical aims to familiarise you with a solution of Fick's Laws of diffusion by studying the diffusion of carbon into austenitic iron. The treatment makes the simplifying assumptions that the diffusion coefficient,  $D$ , is independent of concentration and the surface and bulk concentrations are maintained constant. The quantitative analysis of microstructures will allow you to determine  $D$  values from solute profiles. You will also estimate the activation energy for carbon diffusion.

##### **Skills**

- Heat treatment (pack carburisation) in furnaces will be demonstrated.
- The microscopy will require interpretation of some complex microstructures.
- You will gain experience in the use of image processing software for quantitative metallography.
- Results will be processed by curve fitting; you will need to use spreadsheet or Matlab tools to do this, according to your choice.

##### **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

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there. If metallographic preparation is done, 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.
2. Metallographic sections have been prepared. You will be provided with digital images of the structures from different experimental conditions so that quantitative measurements of phase areas/volumes different depths can be made using 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 Laws. The results will also be used to estimate the activation energy for carbon diffusion.
5. You will need to plan your work and select suitable data so that sufficient 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 samples may contain a small amount of pearlite in their bulk to due variations in the carbon content).

Pack carburisation 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.
- The crucible is placed in the furnace for up to 4 hours 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, but ensures equilibrium microstructures.

### **Metallography**

The heat-treated samples have been cut in half transversely and mounted, then ground, polished and etched for examination.

- After grinding, which removes the distorted metal from sawing during coarse grinding, and polishing, the samples have been

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etched in 2% Nital. It is important to 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 was chosen to be sufficient to show the structure clearly across the whole carbon profile.

- The samples have a 'case' of carburised iron of uniform depth around the whole circumference. They have been cut to examine the mid-section metallographically, and not the end faces. 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**

The objective is to obtain the carbon concentration profile, which you can analyse to obtain the diffusion coefficient for carbon.

This is done by recording optical images of the etched samples, which will then be analysed to obtain the proportions of the microstructure constituents, which depend on the carbon concentration.

There are samples from up to six different carburisation conditions. You do not need to analyse images from all of these. It is expected that you will obtain data by obtaining a suitable set of images from at least **two** conditions.

Instructions for image analysis are given in Appendix A.

- In the images, select rectangles parallel to the surface at regular intervals and measure the proportions of each constituent by

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selecting the areas in each rectangle that are above, or below, a chosen threshold.

- You need to think carefully about the size and position of these rectangles, taking the observed microstructure into account, and consider the effects of this on your measurement uncertainty.
- Similarly, you need to think carefully about the magnification of the images that you choose to analyse.

In principle, the image analysis should be able to estimate the proportion of proeutectoid and eutectoid constituents 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 unless you are confident in your identification of the microstructure constituents.

Using the iron-carbon equilibrium phase diagram, you then need to obtain data for the atomic % carbon against depth.

Advice on the calculations and data processing needed to obtain the carbon concentration profile is given in Appendix B.

Before you start the analysis, think about which samples will give you the data to most accurately measure the carbon concentration profiles, which you will need to obtain values of carbon diffusivity and the activation energy for diffusion.

## **Analysis of Results to obtain Carbon Diffusivity**

If we make the assumption that diffusivity,  $D$ , can be treated as a constant and put constant surface concentrations as a boundary condition, Fick's laws can be solved to give:

$$C(x, t) = C_s - (C_s - C_0) \operatorname{erf} \left( x / 2\sqrt{Dt} \right)$$

You may assume that the carbon content at the outer edge of the sample ( $C_s$ ) 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 book (e.g. Bhadeshia – see Bibliography). The bulk concentration,  $C_0$ , can be estimated from the bulk microstructure of your samples.

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

1. A simple 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 ( $\operatorname{erf}$ ) 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.
2. Another approximate way, if the surface concentration is uncertain, is to take the total case depth as roughly  $2\sqrt{Dt}$ .
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. The

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sensitivity of your analysis to variations in  $C_0$  can also be considered.

## **Bibliography**

Iron-Carbon equilibrium phase diagram:

Bhadeshia, H. K. D. H., and R. W. K. Honeycombe. Steels : Microstructure and Properties. 3rd ed., Elsevier, Butterworth-Heinemann, 2006.  
<http://solo.bodleian.ox.ac.uk/permalink/f/n28kah/oxfaleph000496200>

A short discussion of carburising and diffusion:

Porter, David A., et al. Phase Transformations in Metals and Alloys. Third ed., 2009.  
<http://solo.bodleian.ox.ac.uk/permalink/f/n28kah/oxfaleph021907716>

A succinct treatment of the relevant maths:

Christian, J. W. The Theory of Transformations in Metals and Alloys. 3rd ed., Pergamon, 2002.  
<http://solo.bodleian.ox.ac.uk/permalink/f/n28kah/oxfaleph000985500>

You are recommended to review all of the above.

A fuller treatment of diffusion:

Shewmon, Paul G. Diffusion in Solids. Second ed., 2016.  
<http://solo.bodleian.ox.ac.uk/permalink/f/n28kah/oxfaleph021933826>

The following (rather old, but relevant) are worth reading.

Tibbetts, Gary G. "Diffusivity of Carbon in Iron and Steels at High Temperatures." Journal of Applied Physics, vol. 51, no. 9, 1980, pp. 4813–4816  
[http://solo.bodleian.ox.ac.uk/permalink/f/1lj314/TN\\_aip\\_complete10.1063/1.328314](http://solo.bodleian.ox.ac.uk/permalink/f/1lj314/TN_aip_complete10.1063/1.328314)

Smith, R.P. "The Diffusivity of Carbon in Iron by the Steadystate Method." Acta Metallurgica, vol. 1, no. 5, 1953, pp. 578–587.  
[http://solo.bodleian.ox.ac.uk/permalink/f/1lj314/TN\\_elsevier\\_sdoi\\_10\\_1016\\_001\\_6160\\_53\\_90088\\_1](http://solo.bodleian.ox.ac.uk/permalink/f/1lj314/TN_elsevier_sdoi_10_1016_001_6160_53_90088_1)

## Reporting

**The required report** is your lab book.

You should include in this a representative image of one sample, accompanied by explanations of the structure, a graph (or graphs) reporting the carbon content/distance data for the analysed samples, a table summarising your  $D$  values (obtained by the three different methods described above), and the uncertainty in these values.

Use your data to obtain a value for the activation energy of carbon diffusion, and report the uncertainty in this value.

In your lab book, comment on the following:

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. How do your values of  $D$  and the activation energy compare with literature values? (Take due account of your estimate of the uncertainty in your measurement).
3. The analysis assumes  $D$  is constant with carbon content. How and why does theory predict  $D$  changes with carbon content. Do your data agree with this? What is the analysis method by which the value of  $D$  for any carbon content could be obtained from an accurate carbon concentration curve?

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## Appendix A: Image Analysis

You can download the free software (**Fiji** or **ImageJ**) from [imagej.net](http://imagej.net)

### Using Fiji or ImageJ to Measure the Area Fraction of Pearlite

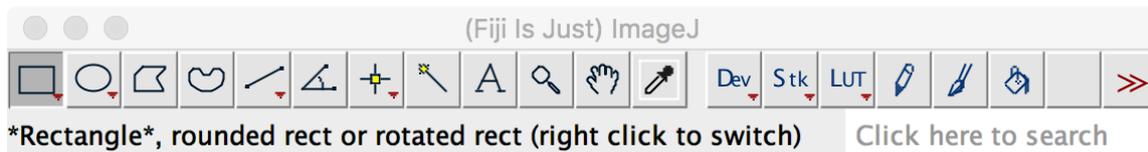
#### *Open Fiji (or ImageJ) and import the image file*

Open **Fiji**, which may also be called (**Fiji is just**) **ImageJ**. The icons are shown in Figure 1. Both are essentially the same software.



*Figure 1: Icons for Fiji and ImageJ*

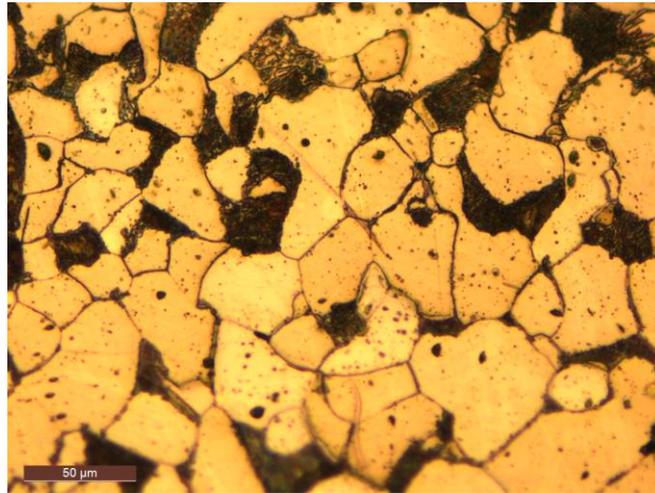
Open your image within the software. You can usually do this by dragging the image file onto the toolbar (Figure 2). Or, choose the menu sequence **File > Open** and then select the image file from the file browser.



*Figure 2: Fiji/ImageJ Toolbar. The 'rectangular selections' tool is chosen.*

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You will then have a colour image (e.g. Figure 3) to work with.



*Figure 3: Example image. The pearlite is dark (as are the grain boundaries). This image is recorded at a higher magnification to show the detail. You may find a lower magnification is more useful for the data acquisition in this laboratory.*

### **Convert Colour to Greyscale**

It is usually easier to threshold and segment images if they are monochrome or 'greyscale', rather than colour (e.g. RGB).

Greyscale images can be 8 bit (grey intensity from 0 to 255) or 16 bit (grey intensity from 0 to 65,535). Usually, 0 is black and the highest number is white, but it can be the other way around. For most purposes, 8 bit is quite sufficient.

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Change the image type chose **Image > Type** and select **8 bit** (Figure 4)

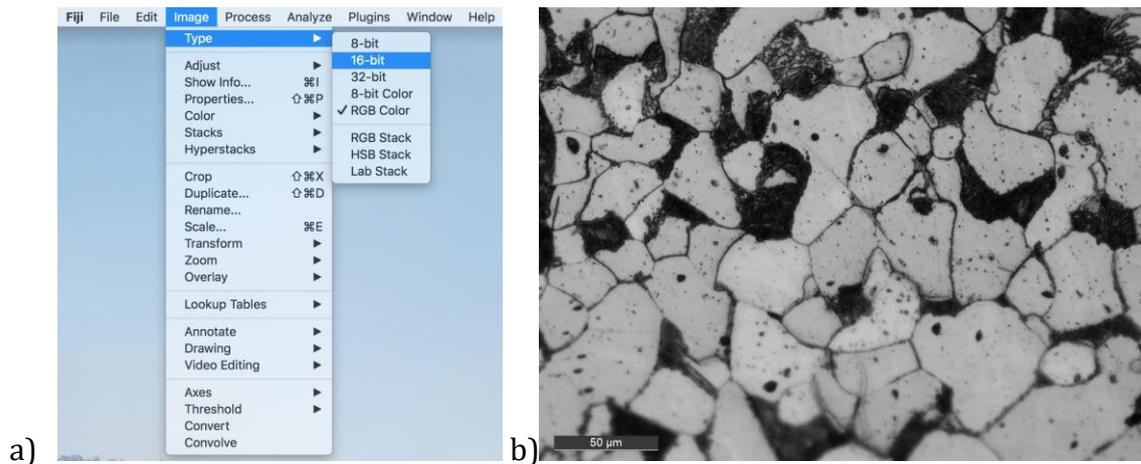


Figure 4: a) **Image > Type** menu commands to convert image type to '16 bit' or '8 bit' greyscale from 'RGB color'; b) converted greyscale image.

## The Greyscale Histogram

You can inspect the histogram of greyscale intensities by selecting your image (click on it) and then using the **Analyse > Histogram** menu commands. This creates a chart of the number of counts of each greyscale level, and also some useful statistics.

The histogram of greyscale intensities in the example image (Figure 5a) shows a good range of intensities (a bit more illumination could have been used in the original image). There is a large peak for the brighter ferrite, and a smaller peak for the darker regions that are mostly pearlite.

If your histogram is mostly to the low or high end of the 0-255 range (e.g. Figure 5b), then it is under or over-exposed and you may not be able to segment it reliably. In this case, 0 is black and 255 is white. It can be the other way around, and the principles described here apply anyway.

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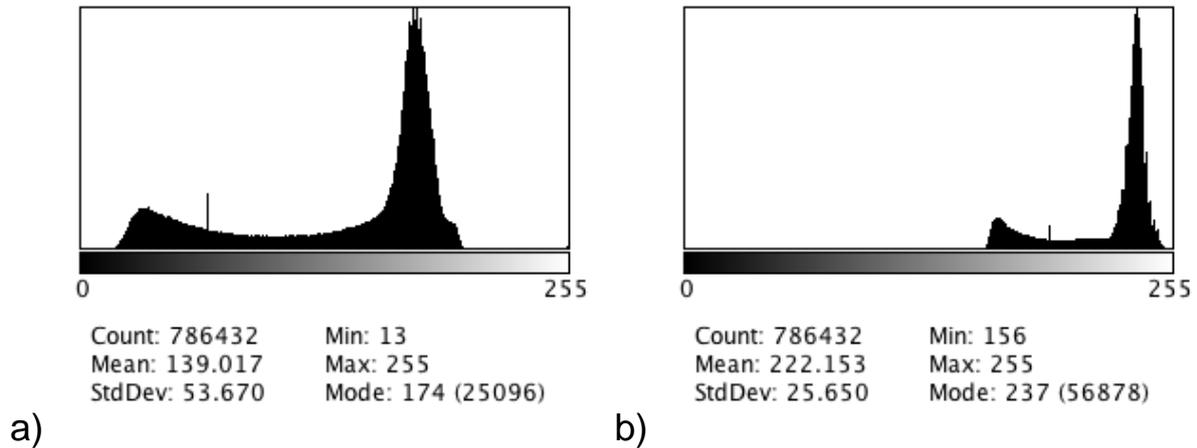


Figure 5: Example histograms of greyscale for a) quite good image and b) over-exposed image.

### Using Thresholds

To separate regions of the image that are within a chosen threshold greyscale range, select your image (click on it) and then use **Image > Adjust > Threshold**. This will open a window in which you can drag sliders to define the range of grey levels (Figure 6).

Here we want to select the dark regions, so the lower end of the range is '0' or black. The upper range selected for this image is '77'.

Click on **Apply** when you are satisfied with the chosen value. This will create a binary image (Figure 7a), with only two colours (0 and 255 greyscale), as shown in its histogram (Figure 7b).

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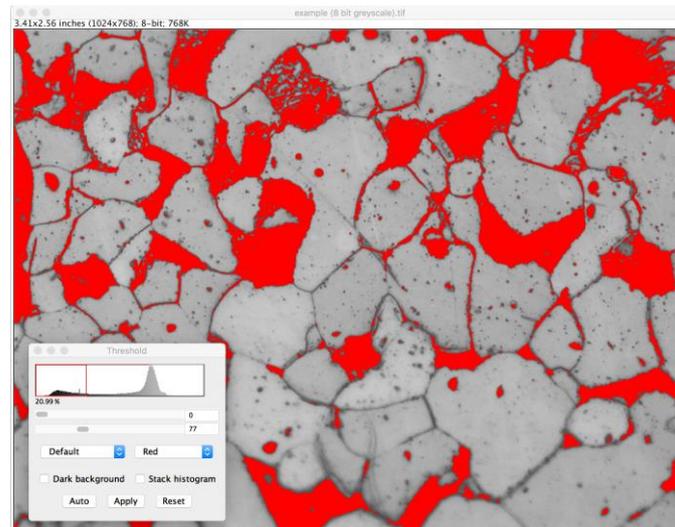


Figure 6: Example of image segmentation to select the dark regions of the image. Here, 21% of the pixels are in the selected range of intensity

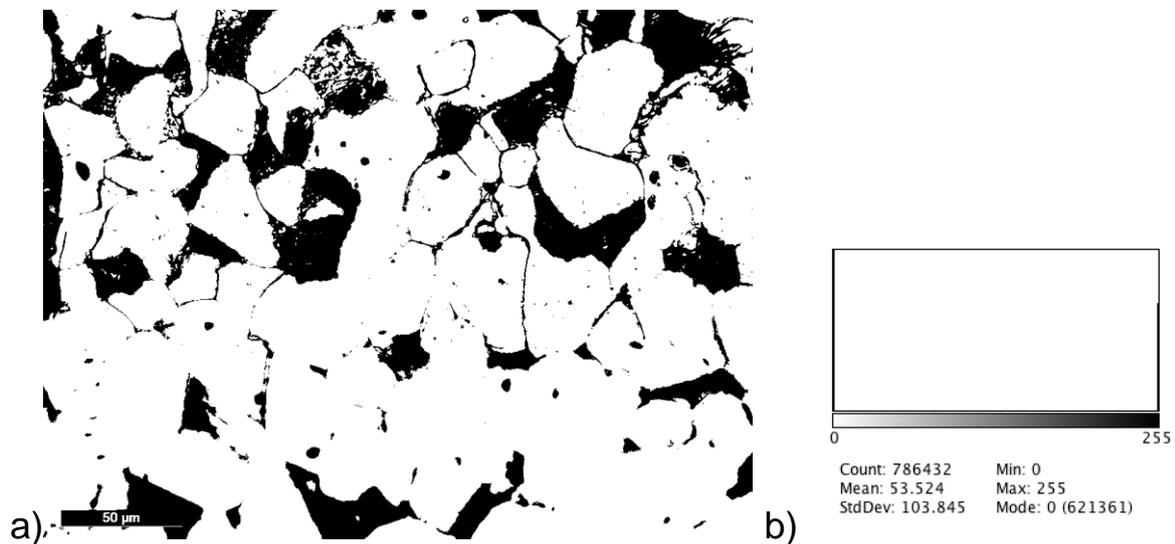


Figure 7: a) Segmented image after threshold selection and b) resulting histogram that has peaks at 0 and 255 only and nothing in between

### Measuring the Thresholded Area Fraction

To obtain the fraction of the image area that has been selected using the threshold, a simple method is as follows:

Choose **Analyze > Set Measurements...** and click the **Area Fraction** and **Limit to Threshold** checkboxes (Figure 8a). This sets a preference to measure only the highlighted pixels within the rectangular selection you made. You can also select **Area**. Press **OK**.

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Select the **Rectangular Selections** tool in the Fiji toolbar (Figure 2) and drag a rectangle over the region that you want to measure (Figure 8b).

Choose **Analyze > Measure** to measure the area covered by the black pixels in the rectangle. You may need to choose **Window > Results** to bring the Results window forward (Figure 8c).

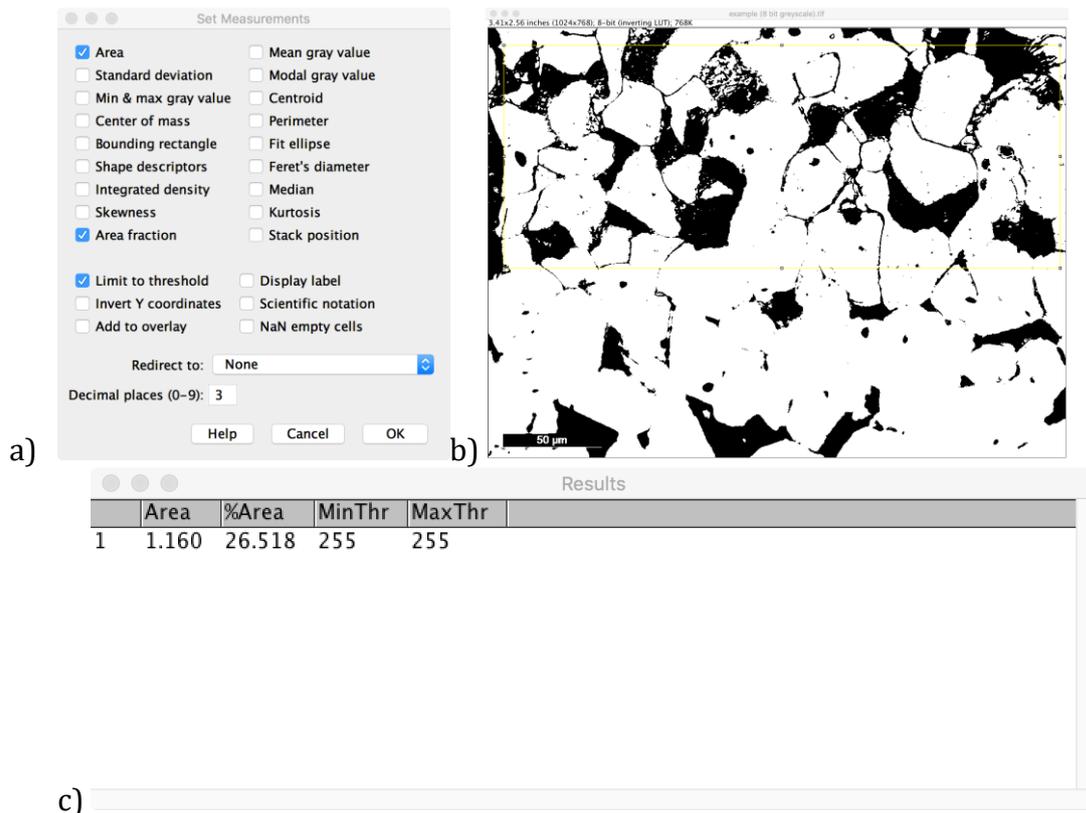


Figure 8: Example measurement. The area fraction in the chosen threshold range within the marked rectangle is 26.5%

Alternatively, you can get the fraction of pixels below the threshold in the whole image, directly from the threshold tool (see the example in Figure 6).

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## **Using Fiji/ImageJ to Stitch Images**

If you want to stitch multiple images to create a montage (i.e. a single image), it is possible to do this using the image acquisition software of the microscope. It is also very easy to do this using FiJi/ImageJ.

To stitch images using FiJi/ImageJ: Put a sequence of overlapping images into a folder (i.e. a 'directory'). Via the **Plugins** menu, select **Stitching > Grid/Collection stitching**. Choose the menu options **Type "unknown position"** and **Order "all files in directory"**, and press **OK**. The default parameters should be sufficient, but don't forget to select the option to **Display Fusion**. **Browse** to find your data, and then **OK**.

This will give you a single image, stitched from the individual images, that may be easier to analyse.

## **Going Further**

FiJi/ImageJ is a very powerful image processing tool that is designed for automation and batch processing of large numbers of images to obtain quantitative data. You don't need these capabilities for this laboratory class, but you may like to explore what can be done. You will find many guides on the internet, and also on the software homepage: **imagej.net**.

The software is free and open source<sup>1</sup>, and you can download a copy from the software homepage to use on your own computer.

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<sup>1</sup> Schindelin, J.; Arganda-Carreras, I. & Frise, E. et al. (2012), "[Fiji: an open-source platform for biological-image analysis](#)", *Nature methods* **9(7)**: 676-682, [PMID 22743772](#), doi:[10.1038/nmeth.2019](#)

## **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 0.02 wt%. The carbon content of cementite (Fe<sub>3</sub>C) 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 (e.g. a value between 0=black and 255=white). If the ferrite is the light phase, the proportion above the chosen threshold can be used to calculate the area fraction of ferrite (you should consider how your choice of the segmentation threshold gives an uncertainty in this measurement). Assuming a binary microstructure, the area fractions of the other constituents 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 ( $A_{wt\%}$ ) of constituent *A* with density  $\rho_A$  and volume fraction  $A_{V\%}$  is calculated as below.

$$A_{wt\%} = \frac{A_{V\%}\rho_A}{A_{V\%}\rho_A + B_{V\%}\rho_B}$$

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The approximate densities of pearlite, ferrite and cementite are 7.5, 7.9 and 4.0 g/cm<sup>3</sup>, 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,  $A_{at\%}$ , is obtained from the weight concentrations using equation below, where  $A_{atom}$  and  $B_{atom}$  are the atomic weights of elements  $A$  and  $B$ . The atomic weights of iron and carbon are approximately 55.9 and 12.0 respectively.

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

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

## **Diffusion and the Error Function**

A simple way to estimate the diffusion coefficient is to apply Fick's laws to predict the concentration profile, which is described using the error function, and compare this to your data. Assume an initial value of the diffusion coefficient,  $D$  and then adjust this to get the best fit.

You can judge the best fit by eye, but you should consider more quantitative ways of comparing the data and prediction to improve the fit. 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.

The solution from Fick's Laws, for the simple case of diffusion over time  $t$  in one dimension  $x$ , with constant diffusion coefficient  $D$  and fixed boundary concentrations  $C_s$  and  $C_0$ , is given as

$$C(x, t) = C_s - (C_s - C_0) \operatorname{erf} \left( x / 2\sqrt{Dt} \right)$$

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

$$\operatorname{erf}(z) = \frac{2}{\pi} \int_0^z e^{-y^2} dy$$

The function **ERF** (in Excel) and **erf** (in Matlab) can be used to calculate the Error Function,  $\operatorname{erf}$ .