CHAPTER 9: MICROSCOPY

9.1 Introduction

The magnetic susceptibility analyses of the various slag and residue samples in the preceding chapters showed each set of samples to have a range of susceptibility values. The three samples within each set which corresponded to the minimum, mean and maximum values of susceptibility in the range measured for that set were selected for microscopic examination to determine the explanation for this range of values.

It was considered that the principal reason for the range of susceptibility values was the variable amount of total iron content present in the sample material and the form in which the iron content could be found, such as free metal, one or more of the common oxides or reacted with silica or alumina, these being major oxides of the gangue material with which the iron came into contact.

9.2 Selection and preparation for microscopy

A total of 42 samples were selected and a morphological examination of each sample was carried out as described in Chapter 2, section 2.7. The samples were obtained from the following locations:

Iron smelting slag	Myers Wood, W. Yorkshire
	Stingamires, N. Yorkshire
Blast furnace slag	Bretton, W. Yorkshire
	Rievaulx, N. Yorkshire
	Sowerby Bridge, W. Yorkshire

Lead smelting slag	Botchergate, Carlisle
	Grinton Smeltings, N. Yorkshire
	Pentre Farm, Flint
Glass production residues	Hutton Common, N. Yorkshire
	Knightons, Surrey
	St. Aidan's, W. Yorkshire
Glass production crucibles	Knightons, Surrey
	St. Aidan's, W. Yorkshire

Thick sections were cut and the sub-samples were prepared for microscopy following the method in Chapter 2, section 2.8. Table 9.1 lists the samples and the corresponding susceptibilities, and the morphological data are presented in Appendix 55.

9.3 Optical microscopy

Examination under reflected light allowed further assessment to be made of the mounted sub-samples through the observation and determination of different mineral and free-metal phases (usually distinguished by varying shades of grey, and bright white/cream, respectively), using the procedure in Chapter 2, section 2.8.1. Images were taken of areas typical of each mounted sub-sample; the optical microscopy data and images are shown in Appendix 55. Examples of the morphological and optical microscopy data from Appendix 55 are shown in Figures 9.1 to 9.5, one each from the five sample categories in Table 9.1.

9.4 Scanning electron microscopy

After carbon coating, the mounted sub-samples were further examined using a scanning electron microscope (SEM) as described in Chapter 2, section 2.8.2. The image of each

sub-sample was scanned for features typical of the whole microstructure and two of these features, designated as sites of interest, were selected for analysis; within each site of interest, two areas and two or more spot locations (hereafter referred to as phases) were chosen for examination. Analysis of the resulting spectra was carried out using the software described in Chapter 2, section 2.8.2. All the SEM images and analysis data for iron smelting slag, blast furnace slag, lead smelting slag, glass production residues and glass production crucibles are presented individually in Appendices 56 to 60. Examples of the data from these Appendices are shown in Figures 9.6 to 9.10, one each from the five sample categories in Table 9.1.

9.5 Morphology and microscopy results summary

The purpose of these investigations, particularly SEM, was to determine the iron content of the various slag and residue sub-samples, and as a consequence, the individual sample descriptions and analyses will not be commented on in depth. A brief description of each sub-sample spectrum and the corresponding iron content are given in Tables 9.2 to 9.6. An average of the four area spectra iron contents was calculated for each sub-sample; this average value was then compared with the magnetic susceptibility of the original, pre-sectioned sample (see section 9.2, and Tables 9.1 and 9.7). An overall summary of the sample group analyses is given as follows.

The Myers Wood (<2000 x 10^{-8} m^3 kg^{-1}) and Stingamires iron smelting slags had compositions which are characteristic of medieval iron making, i.e. a dense, dark brown/grey/black material with an iron oxide (wüstite) dendritic structure and an iron silicate (fayalitic) composition, both contained in a glassy phase. Metallic iron prills of variable quantity and size are present, sizes varying from 3 to 50μm in diameter; there is occasional evidence of hercynite (see Powell *et al*. (2002) for a comparative description

of the Kyloe Cow Beck iron smelting slags). The average iron content ranged from 11.0 to 54.6 %wt Fe. The Myers Wood (>2000 x 10^{-8} m^3 kg^{-1}) samples had similar morphologies and microscopic results but no dendritic iron oxide structures; a greater quantity of metallic iron prills were observed in the optical examination. The average iron content ranged from 11.0 to 75.0 %wt Fe.

The blast furnace samples were of a grey/green to black opaque material and an almost featureless glassy composition with no dendritic iron oxide structures. Most of the samples had no fayalitic or hercynitic phases but all had a substantial quantity of metallic iron prills, ranging in size from 3 to 19μm in diameter. The average iron content ranged from 0.6 to 9.2 %wt Fe.

The lead slag samples from Botchergate and Grinton Smeltings were of a dense, grey/black material whilst the Pentre Farm samples were lightweight and yellow/green in colour; all had some degree of surface degradation from lead carbonate. All the samples consisted of an almost featureless lead silicate glassy composition containing small quantities of blocky/angular phases (Botchergate), considerable quantities of needles, laths and dendritic features (Grinton Smeltings) or large angular phases (Pentre Farm), each with a variable combination of barium, fluorine and zinc components depending on sample source. In addition there were examples of glassy phases (with traces of barium, fluorine, lead and zinc) and “prills” of silica. The average iron content ranged from 1.1 to 8.9 %wt Fe.

The medieval/post-medieval glass residue samples from Hutton Common and Knightons were of a dense, light to dark green mainly translucent material with some surface degradation and had an almost featureless glassy composition containing some

blocky/angular phases and prill-like inclusions. All the samples were typical of silica-lime-sodium glasses, with associated potassium, aluminium, magnesium and manganese components, and traces of sulphur and chlorine. There were varying proportions of some of the elements, e.g. aluminium and magnesium, depending on the location of the glass production sites and, therefore, the sources of the raw materials. The less dense, 18th Century St. Aidan's samples had analyses similar to Hutton Common and Knightons, but with a greater sulphur content, which might be indicative of the fuel used in the glass furnaces, i.e. coal instead of wood. The average iron content of all the glass residue samples ranged from 0.2 to 2.8 %wt Fe.

The dense, yellow/grey glass production crucibles were made of a porous fabric consisting of an even distribution of large grained minerals interspersed with voids of variable size depending on sample. All the samples consisted principally of a silica/alumina mineral with traces of potassium, magnesium, calcium and titanium. Some of the samples contained additional "prills" of silica and zirconium. The average iron content ranged from 0.9 to 1.6 %wt Fe.

Comparisons with other research analyses are not made, being outside the scope of this study, but the reader is directed to the following publications for comparative analyses of slag and other material: iron smelting slags - Joosten *et al*. (1997), Mahany *et al*. (1982), McDonnell (1988), Morton and Wingrove (1972), Photos-Jones *et al*. (1998); blast furnace slags - Crossley (1972), Crossley (1995), Linsley and Hetherington (1978); lead smelting slags - Murphy (1992), Murphy and Baldwin (2001), Smith and Murphy (2003), Smith (2006); glass production residues and crucibles - Bridgewater (1963), Douglas and Frank (1972: 96-97), Hurst Vose (1994), Jackson *et al*. (2003), Kenyon (1967: 39), Mortimer (1993), Welch (1997), Wood (1965).

9.6 Discussion

The comparison between average iron content and magnetic susceptibility is shown in Table 9.7 and illustrated in Figures 9.11 to 9.15. It was anticipated that there would be a correlation between iron content and magnetic susceptibility, i.e. the higher the iron content of a sample, then the greater the susceptibility. However, it can be seen from these figures that this correlation does not entirely hold across the whole range of sample material. The lead smelting samples (Figure 9.13) and the glass production residues and crucibles (Figures 9.14 and 9.15) for the most part exhibit this iron content/magnetic susceptibility relationship. The Grinton Smeltings mean susceptibility sample (Figure 9.13) is considered to be unusual and may not be truly representative of the mean of that sample group's susceptibility range. For both the iron smelting and blast furnace slag samples, the correlation only holds for the minimum and mean values from their respective susceptibility ranges. The six samples representing the maximum susceptibility values do not have a corresponding high value of average iron content, as Figures 9.11 and 9.12 indicate. Figure 9.16 shows the predicted variation of average iron content with changes in the mineral composition of iron smelting slags; the shaded area illustrates the effect on the average iron content of increasing quantities of free metallic iron contained in the slag. A similar variation is predicted with blast furnace slags, although the basic mineral composition is significantly different, being essentially a glassy phase. Where Figure 9.16 shows the mineral composition to contain free metallic iron (in the form of prills *c*. 3 to 50μm in diameter or discrete areas of metal) the average iron content is predicted to increase to high values concomitant with the increased susceptibility of the slag material; Table 9.7 indicates that this is not the case for the high susceptibility slag samples.

Many iron compounds have relatively low susceptibilities compared to the more usual or more abundant oxide compounds, e.g. fayalite (χ = 5 to 130 x 10^{-8} m^3 kg^{-1}), fayalitic olivine (χ = 36 x 10^{-8} m^3 kg^{-1}) and wüstite (χ = 100 to 1000 x 10^{-8} m^3 kg^{-1}). It is possible for a sample which has a high proportion of fayalitic material in its structure, iron smelting slag for example, to have a relatively low magnetic susceptibility but at the same time have a high value of iron content as measured by SEM analysis.

In the foregoing analysis summarised in section 9.5, "low" susceptibilities corresponded to "low" average iron contents, suggesting a near-uniform dispersal of iron compounds throughout the relevant samples. However, "high" susceptibilities did not necessarily correspond to "high" average iron contents, as "low" average iron contents were still measured in several of the samples, particularly the iron smelting and blast furnace slags. The reasons for this are not clear and investigations are beyond the scope of this research. However, a potential reason is suggested: where "high" susceptibility iron compounds are distributed unevenly in discrete areas throughout the sample, it is possible for the thick section, removed from the sample for mounting, to miss some or all of these discrete areas, leading to an imprecise measurement and an apparent discrepancy between iron content and susceptibility.

The presence of iron compounds in iron smelting and blast furnace slags is self-evident, being derived from the iron ore. However, the source of the iron content in lead smelting slags, and glass production residues and crucibles is less obvious. Analysis of the slags from the lead smelting sites on the lower slopes of Calver Hill in Swaledale, N. Yorkshire, showed that they were mixed silicates containing lead, barium and calcium but with lesser quantities of potassium, sodium, iron and aluminium (Smith and Murphy

2003). Hall and Photos-Jones (1998) note that iron sulphides often accompany other metal sulphides, such as galena (PbS) and sphalerite (ZnS).

Where sand is used as the source of silica in the production of medieval and post-medieval glass, iron is often found as an impurity in glass (Tyson 2000: 5; Henderson 2001: 474); iron can also be introduced through its association with manganese in the wood ash used as an alkali in "forest" glasses (Henderson 2000: 34). As a consequence, the presence of iron in glass is significant in that it has implications not just for the coloration but also for the magnetic characteristics of the glass product and any associated waste material (Henderson 2001: 474). It is feasible that different sources of sand will contain different levels of iron impurity, a circumstance which is apparent from the results shown in Table 9.7.

9.7 Conclusions

The results of the microscopic examination of the iron smelting, blast furnace and lead smelting slags, and the glass production residues and crucibles demonstrated that there was a variable quantity of total iron content present in the sample material. When this iron content was in the form of relatively low susceptibility material, there was a correlation between iron content and susceptibility. However, when the iron content was in the additional form of discrete, relatively high susceptibility material, such as prills of metallic iron, there was no correlation. This anomaly is due to the sections taken for microscopic examination containing very little or none of this discrete material.

The microscopic examination procedure, whether optical or scanning electron, has been shown not to be as successful as expected in the determination of total iron content and corresponding magnetic susceptibility. A more appropriate method of selecting the

location of thick sections from the parent samples should be sought, in order to have a better representation of total iron content in the sub-samples.

A possible solution for ensuring that discrete areas of high susceptibility material are contained within a section would be to radiograph each high susceptibility sample, to determine where the discrete areas were located within the sample and thus enable appropriate positioning of the section. It is recognised that this procedure could be resource intensive and perhaps only suitable in specific instances.