

# ON THE CLASSIFICATION OF ANCIENT SLAGS BY MICROSTRUCTURE EXAMINATION

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## Abstract

In this paper we will point at the possibilities of using the microstructure of iron-slugs for the determination of a possible main type of production process used in early iron-making on a site, where production is indicated by slag remains in suitable amounts. For that purpose, four main types of furnace are presumed and shortly explained with regard to significant process details in heating, ore reduction and slag formation. The resulting slag microstructure is discussed for three of them. The leading structure element for identification is found to be micrograins of metallic iron. Concluding comments on the reliability of the method in comparison to certain calculation methods used by other workers are given in the final part.

## Introduction

In metallurgical processes liquid slags form as by-products. Compared to modern conditions the ancient slags are mostly very different not only in chemical composition but in structure appearance and the general lack of homogeneity. Here, only the processes for iron-ore reduction will be dealt with. In many remains from such processes only the slag is left as evidence of an activity. The aim for our work is to show, how microscopical examination of slag samples can be used to identify the type of furnace, which at a certain site has been used to produce the findings. We will shortly outline the technological and metallurgical background, show some diagrams and photographs and discuss significant details for the actual main types of reduction process and some resulting microstructure characteristics. A comment will then be made on another way of searching into the matter by calculation only. Reliability judgements finish the paper.

## Significant features at early processes for iron-making

Of the four main types of furnace actual from metallurgical points of view, the first two required very fine-grained ores such as bog-ores and riversand, while the other two because of water-powered air-blast were capable of smelting rock-ores of coarser size, normally in the order of walnuts or hen-eggs. Regarding furnaces for fine-grained ore the essentials would be:

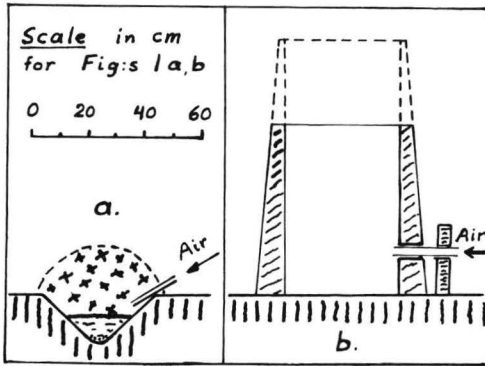


Fig. 1

Fig. 1. Furnaces requiring fine-grained ore. a. The Bowl-Hearth. b. The Bloomery.

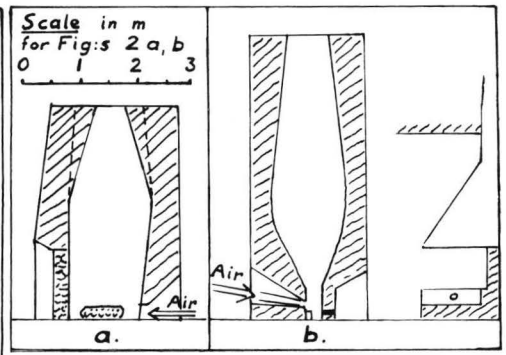


Fig. 2

Fig. 2. Furnaces for smelting coarse ore. a. The High Bloomery («Stückofen»). b. The Blast Furnace with Finery Hearth.

*The Bowl-Hearth*, see Fig. 1 a. The shape is easy to bring about by digging a conical pit. The air-blast can be provided by muscle-power (blow-pipes or bellows). Extremely fine-grained ores, e.g. red-earth, are usable, which has not been successful in shaft-furnaces. The iron has a low carbon content and is obtained as prills of pea-size, or less, after crushing the cold slag. Metal products gather at the bottom center automatically.

*The Bloomery*, see Fig. 1 b. Because of the standing shaft, even if not a tall one, the ore is given prolonged descension time relative the bowl type, which lessens the loss of ore into slag and increases the iron yield. The main product normally is soft iron low in carbon, but carburization may occur, especially when the shaft-height is increased. The air-blast has mostly been supplied by muscle-driven bellows in pairs, sometimes by water-power (18th—19th cent:s), exceptionally perhaps also by natural draught. Heterogeneity in iron and slag properties is usually due to gradients in the temperature distribution causing changes in the conditions for equilibrium in the actual chemical reactions.

Regarding the water-powered higher furnaces capable of reducing rock-ores in coarser piece-size, the following would be most essential:

*The High Bloomery* (Germ. »Stückofen«, Swed. »Styckeugn«, Fin. »Harkugn«.). See Fig. 2 a. A tall shaft of various inner shape resting on a wide, mostly oval or circular hearth accessible through a large front-door, at running closed by a stone wall but at the end of blowing opened for removal of iron and slag and relining before the next run. Main product is a big lump of malleable iron, by-products are pig-iron and slag.

In relation to the lower bloomery, the burden descent is lasting much longer and will result in higher mean temperatures in the burden stack. In addition, the exposition of the iron to carburization will be prolonged so that some iron will be transformed into liquid pig iron.

*The Charcoal Blast-Furnace*. See Fig. 2 b. From the top mouth downwards, the inner width increased until a maximum and then decreased like a funnel into the rather narrow hearth of rectangular shape, where the descending iron and slag collected, highly heated at passing the hot tuyere range »little by little as the sand within an hour-glass« as expressed by Garney and Lidbeck (1816). The tall height, the funnel-shape and the narrow hearth are the significant design features. The produced iron, liquid

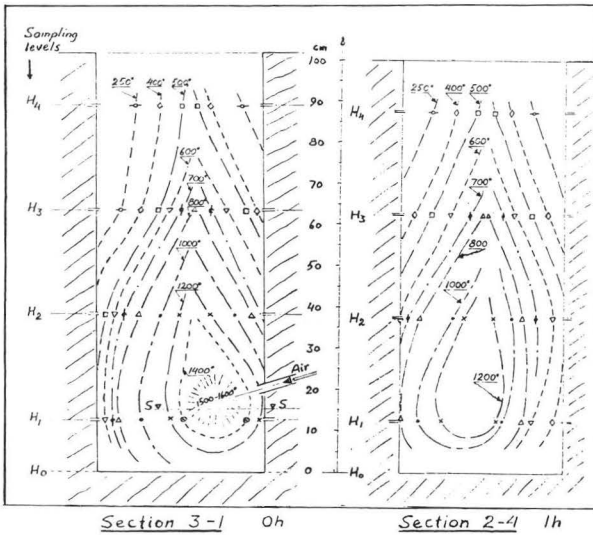


Fig. 3

Fig. 3. Bloomery temperature distribution. Vertical isotherms, perpendicular sections, at start of charging (0 h) and 1 h later.

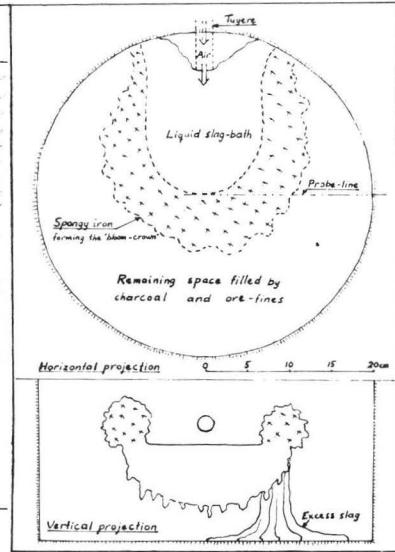


Fig. 4

Fig. 4. In a bloomery a bowl forms along an isotherm embracing a slag bath, where iron grains collect continuously, above which unprotected iron forms the «diadem».

pig iron only, must be refined separately to be malleable, from the very beginning made by oxidation in a specific finery process. Of the early iron-processes the B.-F. was the only one in which fairly homogeneous conditions could exist for the two products collected in the hearth: the iron-well on the bottom and a slag-well on top.

With exception of the iron- and slag-wells on the bottom of the B.-F., just mentioned above, the three other furnace types had one important feature in common, namely the uneven temperature distribution spread out radially from a very hot «blast-focus» in front of the tuyere and ending up at the walls at rather low degree-values giving great influence on reaction constants and equilibrium displacements concerning gas atmosphere and burden phases. The bloomery isotherm diagram in Fig. 3 may serve as an illustration. Other furnaces with one single tuyere behave in a similar way.

In spite of the lacking homogeneity in temperature distribution, compared to modern metallurgical equipment, the early processes had real possibilities to provide temperatures high enough to melt pure iron, melting point  $1536^{\circ}\text{C}$ , contradictory to the hitherto prevailing opinion. In addition to direct measurements, see Fig. 3, there also are other evidences. We have found, namely, that micrograins of iron often occur in habits of a liquid phase. In an experimental study by one of the authors, this has been confirmed by reasons to be presented below and in a forthcoming report, Tholander (in press). Iron micrograins appear as swarms of «dust» formed by mechanical erosion of brittle sponge-iron films covering each piece of ore heated above  $700^{\circ}\text{C}$ . The little mass, in sizes of some millionth of one milligram, of the dustgrains measuring  $20\ \mu\text{m}$  or less in width, makes them able, in the hot gas region, to absorb heat-energy rapidly enough for reaching the melting point very quickly. By descending through the blast-focus as a «rain» of liquid and semiliquid units of pure iron, they then could successively build up compact lumps growing to form solid blooms within a protecting

slag-bath as shown in Fig. 4, deduced from bloomery experiments at the R.I.T. Therefore, the usual explanation saying, that all early wrought iron was formed at about 1200°C only is not correct.

**Slag formation fundamentals. A new explanation**

The conventional explanation of how the slag is formed in the blast-furnace process, and by implication also in the earlier processes, has been simply expressed by Ward (1962) in the following way:

»Fundamentally the B.-F. is a counter-current apparatus in which descending iron-oxide, coke and slag-making materials remove heat from an ascending stream of hot reducing gases. . . . Chemical reduction of the iron oxide also occurs as the charge descends and finally . . . fusion of the reduced iron, some unreduced iron oxide and slag-making materials take place.»

The basis for the following, new interpretation of the course of the slag formation is the microscopical studies we have made on ancient slags during the last ten to fifteen years. Especially the examination of microstructures of samples taken out from the shaft of different furnaces has given information of interest. This study is a part of the recent research project at the R.I.T. already mentioned (Tholander).

Each single piece of ore consists of several small mineral grains, i.e. grains of iron minerals, usually hematite (Fe<sub>2</sub>O<sub>3</sub>) and/or magnetite (Fe<sub>3</sub>O<sub>4</sub>), and grains of gangue material (e.g. SiO<sub>2</sub> and CaO, MgO, MnO, Al<sub>2</sub>O<sub>3</sub> etc.). When the ore-piece descends

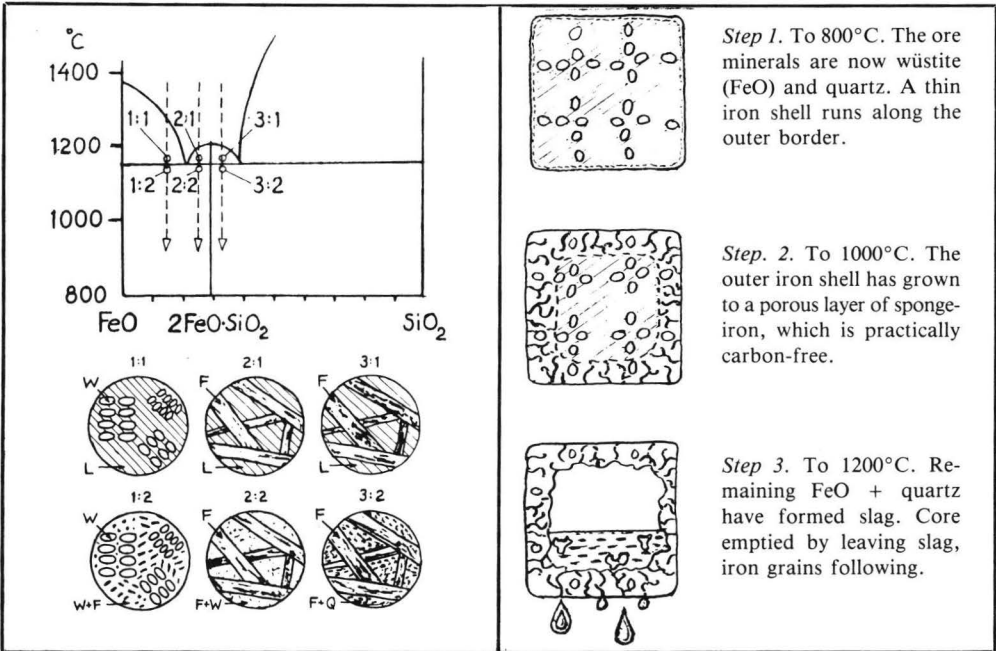
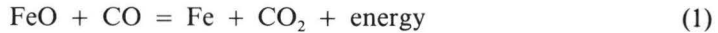


Fig. 5. Phase diagram for the system FeO-SiO<sub>2</sub> Solidification at three concentration cases: (1), (2), (3). Step 1 shows the type of primary crystals expectable, Step 2 gives schematically the final phases in each case. Marks: W = wüstite, F = fayalite, L = liquid, Q = quartz. W + F, F + W, F + Q = eutectic reactions.

Fig. 6. The iron- and slag-formation story told in 3 heating-steps in a CO-rich gas.

in the furnace, its temperature rises and the iron mineral is reduced by the ascending gas, at first to lower oxides. From about 700°C metallic iron starts to form according to equation (1):



In the surface zone of each piece of ore, the iron mineral is reduced into a layer of spongy metallic iron. When the temperature in the zone next to the reduction zone has reached a temperature of 1175°C, not all of the iron mineral has been reduced to metallic iron. So, in the ore-piece, wüstite (FeO) exists side by side with gangue grains. At this temperature, 1175°C, the system FeO — SiO<sub>2</sub> in Fig. 5, however, has a eutectic, which leads to fusion in the contact surfaces between wüstite (FeO) and quartz grains (SiO<sub>2</sub>). That is the start of the slag formation.

The slag drips out of the ore-piece through openings left in the spongy iron shell, descends in the shaft and can at rising temperature gradually dissolve other gangue minerals so that the total amount of slag increases. Finally, the slag is collected into the slag-well in the hearth.

The sketch in Fig. 6 shows visually the slag formation principle described above. The Figs: 7, 8 and 9, showing cross-sections through two ore-pieces in macro-scale and one in micro-scale, do confirm the reality in the described principle. The pieces sectioned in Figs: 7 and 8 belong to the B.-F. campaigns reported by Bohm (1927) and have, after preservation in the department-museum at R.I.T., been reexamined in the recent research project.

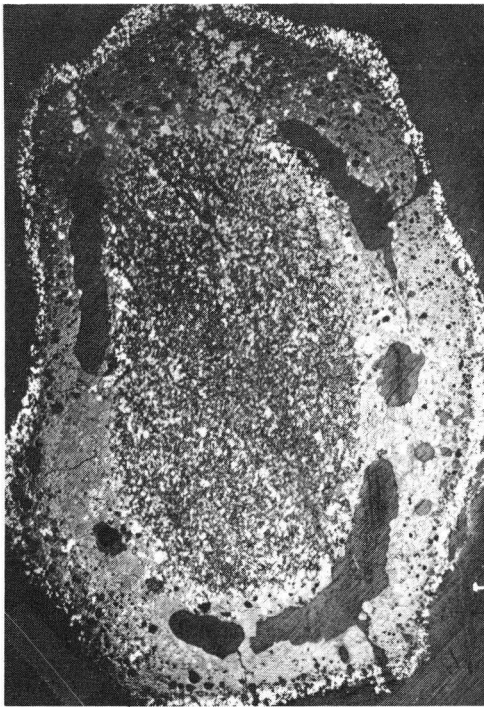
By comparing the starting level for B.-F. slag formation indicated by microstructure examination with the level for 1175°C (12 feet) recorded by direct measurements, it was found that crystallized fayalite occurred on level 8—9 feet with a recorded temperature of 930°—1020°C, in average 975°C. That means an excess temperature inside the ore-piece of 200°C above the surrounding stack, the height difference being 3 feet.

The explanation of that temperature increase within an individual piece of ore is quite simple. Both the ore reduction according to eq. (1) and the fayalite forming reaction are exothermic, i.e. energy disengaging, which gives a natural temperature rise at the reaction front. The phenomenon is of a general nature, but it has not been noticed earlier, as far as we know.

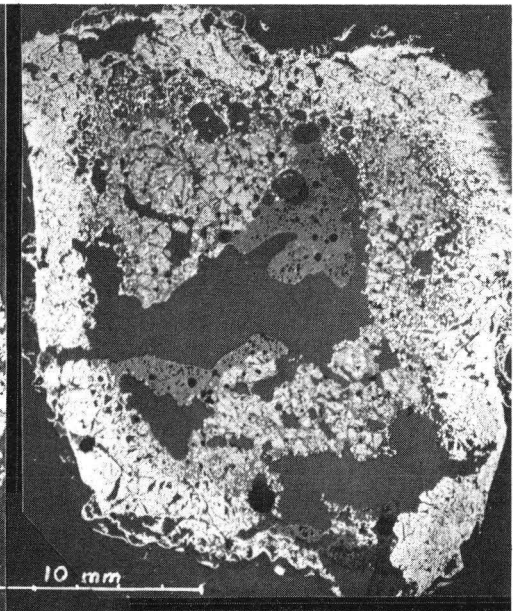
### **Solidification influence on the slag microstructure**

The most common crystallized phases occurring in the microstructure of slags are wüstite (FeO), magnetite (Fe<sub>3</sub>O<sub>4</sub>) and fayalite (2FeO.SiO<sub>2</sub>), see Figs: 5 and 10. In addition, glass occurs without exception. All these phases can appear in the same slag, but in many cases one or more of the first three ones may be missing. Usually the glass is not clean and transparent but contains fine-dispersed fayalite and, locally, sometimes also fine-dispersed wüstite or magnetite. The occurrence of glass and the absence of regular eutectics are due to the cooling rate which for a slag, in practice, is so high that there is no time for a perfect solidification course.

As was the case at the slag formation in the reduction furnace, the system FeO — SiO<sub>2</sub> is the most important one for the discussion of the solidification of a slag. At the diagram in Fig. 5 there is also shown the idealized solidification courses at three different compositions. According to the diagram, primary crystallization should occur of wüstite in case 1 and of fayalite in cases 2 and 3. At about 1175°C two eutectic reactions can take place giving eutectics consisting in cases 1 and 2 of wüstite and fayalite and in case 3 of fayalite and quartz. As Fig. 10 shows, in reality both primary wüstite



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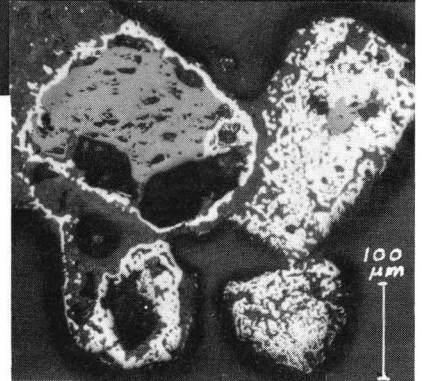
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**Examples on initial slag formation within ore-pieces taken out from furnace burdens:**

*Fig. 7.* Siliceous ore, sunken 10 ft. Swedish charcoal blast-furnace.

*Fig. 8.* Self-flux ore, 14 ft, the same blast furnace as at Fig. 7.

*Fig. 9.* Fine-grained sinter ore, sunken 85 cm in a bloomery of 100 cm height.



9

and primary fayalite can appear in the same slag structure, which is not expected theoretically but practically might be an effect of subcooling. After the formation of wüstite crystals in the hypoeutectic melt, the silica content in the remaining liquid increases and the temperature falls below the eutectic temperature, so that the melt becomes hypereutectic. From this melt fayalite crystals can be formed similarly as at ordinary hypereutectic conditions. Secondary wüstite, magnetite or fayalite often occur instead of regular eutectis, see Fig. 11. A special type of eutectic also is to be seen in Fig. 10, where a combination of fayalite-magnetite appears, probably representing the system  $\text{FeO} - \text{SiO}_2 - \text{Fe}_2\text{O}_3$  and formed at about  $1140^\circ\text{C}$ . The other gangue minerals besides  $\text{SiO}_2$  mainly end up in the last solidified glassy parts of the slag. They usually seem to play a rather passive role at the solidification process.

**Microstructure characteristics assignable to certain processes**

Morton and Wingrove (1969) seem to be among the first to have published micrographs of ancient slags. They introduced a new mode of investigating slags by combining the

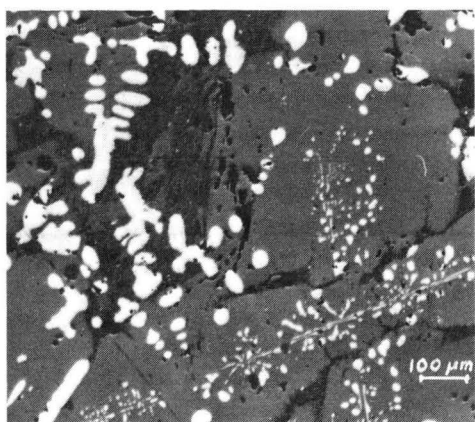


Fig. 10

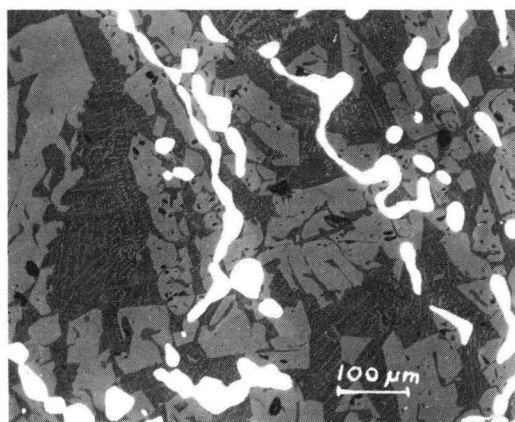


Fig. 11

Fig. 10. R.I.T. smelt No. 13. High-bloomery slag near the air-blast inlet. Coarse wüstite and fayalite, tiny secondary magnetite and glass. White phases: wüstite, magnetite. Grey phases: fayalite, glass.

Fig. 11. Bloomery slag, Västervåla, Västmanland. Primary and secondary fayalite (grey) in glass matrix, dark. Ferritic iron micrograins (white) as «corals» and thread-like fragments of labyrinthine sponge-iron.

determination of microstructure phases with a calculation of the main mineral constituents on basis of the chemical analysis and certain simplifying assumptions. They claimed the main constituents in Roman slags to be FeO, fayalite and anorthite ( $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) and also, that they could determine the average «working temperature» at the production of such slags to have been in the order of  $1150^\circ - 1250^\circ\text{C}$ . In a later work, Morton and Wingrove (1972) found that medieval slags from rich ores behaved similarly to the Roman type, but that the slags from carboniferous and lean ores had constitutions of higher melting points with hercynite ( $\text{FeO} \cdot \text{Al}_2\text{O}_3$ ) and other spinels as dominating constituents. They assumed, however, that the only iron-oxide existing in the slag before tapping is FeO, which cannot always be correct. They also regarded the glass matrix as anorthite. Modern analysis methods have shown that this is not the case. Later on Wingrove (1970) has published excellent micrographs on the appearance in silicate slags of the three iron oxides wüstite, magnetite and hematite. A rich assortment of slag micrographs in eminent performance has been presented by Sperrl (1980), who also considered the occurrence of iron micrograins, though in a quantitative aspect only.

Our microscopical studies are to a great extent made on numerous slag samples originating from archaeological excavations in the Nordic region as well as from own smelting experiments. Besides the normal slag phases we have found, that there often are other types of solid particles occurring in ancient slag. There can be undissolved or partly dissolved iron minerals as in Fig. 12 or quartz as in Fig. 13. Small pieces of charcoal also can be seen. But most important is the occurrence of metallic iron because it offers good possibilities, if considered properly, to contribute to the identification of the type of process from which a slag sample is likely to originate. It then is the occurrence as micrograins of various shape, which has to be noticed as listed below and illustrated as indicated, namely:

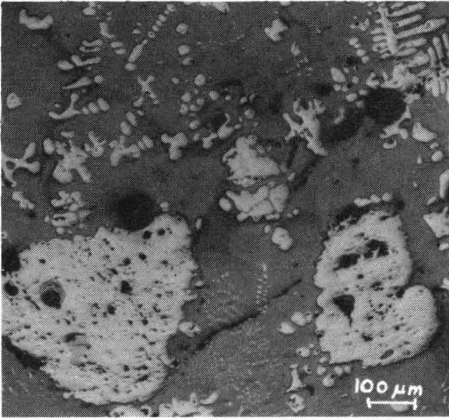


Fig. 12

Fig. 12. R.I.T. smelt No. 4. Bloomery slag with excess oxygen from undissolved iron-ore mineral. Wüstite (grey) in fayalite matrix. Small ore-bits dissolving, big not. Dotty precipitate = sec. magnetite.

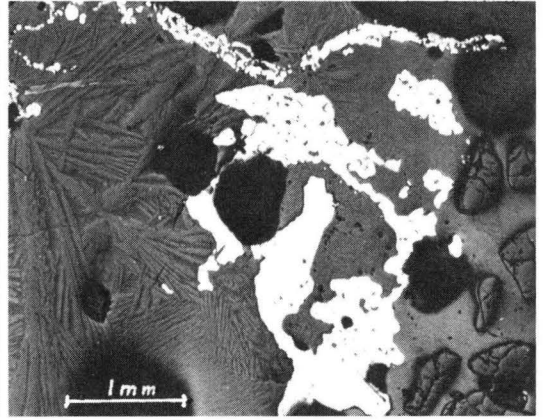


Fig. 13

Fig. 13. R.I.T. smelt No. 18. Bowl-hearth slag with undissolved quartz, glassy matrix and fayalite. Ferritic iron micrograins form compacted large aggregates and slender shell-like structures.

		Fig. No:s
labyrinthic iron	primary formed grains of sponge-iron obtained at gas-reduction	9, 14
coral iron	fragments of labyrinthic iron	11
compacted iron	dense iron areas, irregular shapes	13, 14, 15
globular iron	circular or almost round particles	16, 17
shell-like iron	thread-like sections, often of various thickness	9, 11, 13, 14

Very often *rust* is seen in the slag microstructure. It always consists of corroded iron or iron-corrosion precipitates. The slag itself cannot rust. Sometimes it is possible to recognize the rust as corroded labyrinths or corals. The corrosion is the result of oxidizing reactions between the iron and some water-solution rich in oxygen and penetrating the slag through cracks and shrink-cavities under the pressure of capillary forces. Indirect corrosion-products are precipitates of ferric hydrates formed when water-solutions containing dissolved ferrous salts enter an environment rich in oxygen.

Concerning the classification of slags, we have found that the ordinary bulk slag-structure with its mineralogical phases is not an usable basis for the iron-reduction slags. The only feature worthy to be noted here is that neither wüstite nor magnetite have ever appeared in the microstructure of blast-furnace slags. That does, of course, not mean that a slag without wüstite and/or magnetite must emanate from a blast-furnace. Returning to the *iron-micrograins*, however, the main characteristic types, which we at present find assignable to certain production processes, are the following of which examples are shown in the figures indicated:

		Fig. No:s
Bloomery slags	labyrinths and/or corals	9, 11, 14
High Bloomery slag	labyrinths and/or corals together with circular and almost circular grains	16
Blast-furnace slag	Circular or almost circular iron grains	17



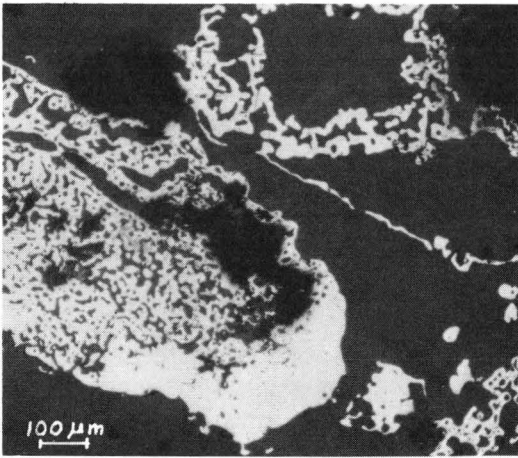


Fig. 14

Fig. 14. Bloomery slag, Rödön, Jämtland. Labyrinthis iron, partially compacted, and thread-like shell sections in a glassy matrix with fayalite dispersion.

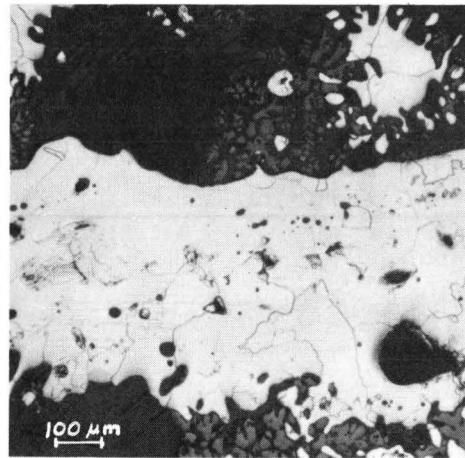


Fig. 15

Fig. 15. R.I.T. smelt No. 1. Compacted ferritic iron in semiliquid and liquid state and solid «corals» gathering in the bloomery slag-bath below the tuyere.

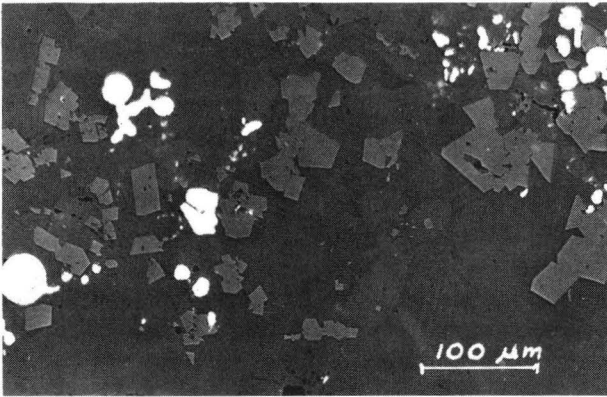


Fig. 16

Fig. 16. High-bloomery slag from Dobryanski, SSSR, about 1887 and a Finnish «Harkugn». Mixed solid and liquid iron-grains, medium carbon content, among olivine crystals in a glassy matrix.

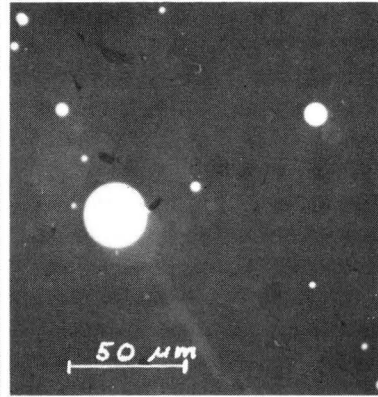


Fig. 17

Fig. 17. Blast-furnace slag, Edske masugn, Gästrikland, about 1870. Globular iron grains of diameters 30—2 μm in a silicate slag of glassy structure.

### Comments on the reliability of actual methods for slag classification

A method for the calculation of an expected mineralogical composition of a specific slag on the basis of the chemical composition was published by Norin (1968) long ago. Lately, a similar method, the «normative» method using a computer, was developed by Serning et al. (1982, 1983), who presume that their method should possess a great

potential for chemical-mineralogical classification of slags. Important difficulties at the use of such methods are, however, the foundation on idealized phase-diagrams and the fact, that the number of slag components often is great and therefore the application becomes complicated. We have, for instance, got quite different results by using on the same slag analysis the methods suggested by Norin (1968) and by Serning et al. (1982, 1983).

One condition for the use of the normative method for classifying must be, that characteristic differences between the »norms» are knit to certain metallurgical processes. It does, in turn, mean that a certain type of furnace must produce a slag of a characteristic chemical composition. Which suppositions do then exist for that requirement?

Generally, the composition of a slag from an iron reduction furnace depends on two factors only, the composition of the gangue and the iron wasted in the process (the part of iron minerals charged, which not is reduced into metallic iron but ends up in the slag). Neither certain types of gangue minerals nor specific iron-yield figures can be connected with any of the four types of reduction furnace dealt with in this paper.

It therefore goes without saying, that the composition of the slag cannot be generally characterized by the type of furnace from which it does emanate. With this elementary reasoning as a background it is impossible to give any credence to the use of »normative» calculations for the classification of ancient slags. On the other hand, the calculation method might be of value in guiding a mineralogic identification of phases observed at microscopical examination of slag structures.

Turning to the question of reliability at the microstructure examination method, there must be pointed out that one factor of uncertainty is the high degree of heterogeneity stated in temperature distribution and, consequently, in the slag bulk-structure. By concentrating the classification main criteria to the occurrence of metallic iron micrograins, however, the method would be independent of equilibrium changes in the slag formation reactions. Shape and state of the iron micrograins are to a great extent bound up with process fundamentals such as furnace design and air-blast supply. That makes the criteria founded on physical realities in each process.

It is recommendable not to rely on a single slag-piece only, but to employ series of samples to obtain reproducible determinations, e.g. a minimum of three, preferably five to ten pieces for each classification task.

## General conclusion

Our general conclusion is, that the method of slag classification by microstructure analysis based on the occurrence of micrograins of metallic iron in the slag, certainly has the capability of usability and development, because it is founded on physical realities.

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