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RESEARCH ARTICLE

Smelting experiments in the early medieval fajszi-type bloomery and the metallurgy of iron bloom

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Abstract

Mankind may have discovered iron several thousands years ago but until the late medieval ages this important raw material was made from the iron ore in a one-step process in the small bloomery furnaces (direct production of iron). The smelting temperature was only about 1100–1300°C which meant that the melting point of the iron was not reached. Due to the relative low metallurgical temperature the product of this ancient technology was a spongy-structured solid iron mass with some unwanted slag. This was commonly known as the iron-bloom. For decades, interest has increased in the ancient metallurgy technologies and a new discipline evolved: The archaeometallurgy. How did the ironworkers make the iron in their small furnaces in the early medieval ages (7-12th cent. AD). During the past two years a team in a collaborated study with archaeologists set out to discover the workings of this ancient technology using experimental archaeology consisting of more than 20 smelting experiments. From these experiments the parameters of the technology (i.e. temperature, gas-composition) were measured and the resulting iron ore, slag and iron-bloom samples were examined (i.e. chemical, metallographic and mineralogical analysis). Based on the results of these smelting experiments, measurements and analysis, it is possible to draw some conclusions regarding the physical-chemical and metallurgical processes of the early medieval iron production.

Keywords

Archaeometallurgy · experimental archaeology · smelting experiment · bloomery · iron bloom

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1 Introduction

To date, more than 300 early medieval bloomery workshops have been excavated in Hungary, most of them by Dr. János Gömöri. Throughout the course of these excavations, many objects were found in connection with the ancient technology, such as: remains of charcoal piles, re-heating pits, iron ore roasting pits and furnaces [1]. The main component of the technology was the furnace itself. There were two types of the early medieval bloomery furnaces located in the Carpathian Basin: The free-standing bloomery and the built-in bloomery. One of the built-in type furnaces was the Fajszi-type (10th century AD). Based on the data of archaeological findings the Fajszi type furnace was approximately 70-100 cm tall and this was built into the side wall of a workshop pit with its full height. The workshop pits were 50-80 cm deep, 3-4 meters wide and were either square or horse shoe shaped pits. There were several furnaces located in the side walls. These furnaces were conical with the inner diameter of the hearth being around 30-40 cm and the inner diameter to the throat was 10-15 cm. On the front side of the furnace there was a 20-30 cm wide hole, which was closed during the smelting process using a breast-wall. A twyer was put into the twyer-hole of the breast-wall and one or two hand-bellows could be connected to the twyer [2].The Fig. 1 shows the typical construction and dimensions of a Fajszi-type bloomery.

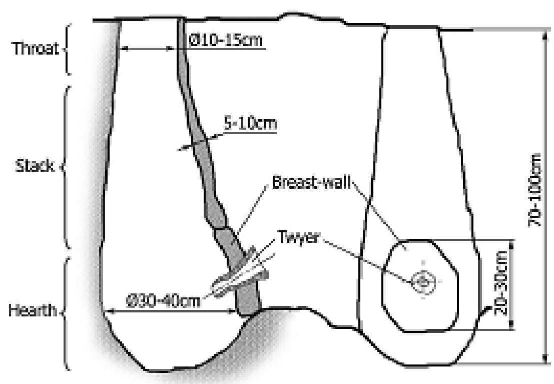


Fig. 1. Typical construction and dimensions of the Fajszi-type bloomery.

2 Experiments

Since the commencement of this project in the summer of 2008, more than 20 smelting experiments have been carried out using experimental Fajszi-type furnaces. The first six were not successful, but in case of the others, iron blooms were obtained. After processing the weight of these iron blooms were approximately 1-2 kg. All the tools, materials and technologies used were considered to be true representations of those used in this period. It was very important to work to be as authentic as possible.

2.1 Workshop pit deepening and furnace building

The first step is to have a workshop pit that has side walls 50-80 cm in height. The desired shape for the furnace can be dug into the side wall, which is then covered with a mixture of sand and clay.The final step is the drying where the furnace must be dried by slow fire in its hearth to avoid the cracks developing. The slow drying process takes about 5-10 hours.The robust construction of the built-in type furnace has one key advantage over the free-standing type, in that, several smelting processes can be carried out and only the breast-wall has to be repaired after each smelting operation.

2.2 Iron ore mining and preparing for smelting

In the early medieval times the ancient foundry men used, what was commonly known as, bog iron ore. The bog iron ore is a type of iron deposit that develops in bogs or swamps by chemical or biochemical oxidation of water solution of iron (Fe^{2+}) [3]. In general, these iron ore bogs contains mainly iron-oxyhydroxides (commonly goethite; FeO(OH)) so they always have more or less hydrate water content. Even today, period iron ore deposits can be found at various locations in Hungary and original iron ore lumps were collected from four of these sites for the smelting experiments: Kék-Kálló valley and Fancsika (near to Debrecen), Somogyszob and Petesmalom (in south-west Hungary).All of these iron ore deposits were found near to a brook or a lake. The common physical property of the iron ore bogs is the brown colour and the porous structure. Due to the porous structure the surface-area-to-volume ratio is large so there is a significant reaction surface for the reduction.After washing and breaking, these iron ore lumps are roasted in a roasting pit which is a 10-20 cm deep, ovoid pit. During the roasting, the iron ore pieces are roasted in wood and charcoal fire.The goethite looses its hydrate water content and becomes hematite. The colour of the originally brown iron ore becomes to red, this colour changing is the indicator of the good roasting process. The end result of the roasting process is a hot mixture of iron ore pieces, charcoal and some wood ash, which is the perfect fuel for the bloomery.

2.3 Iron smelting

Prior to the iron smelting, the furnace is preheated and the roasted iron ore and charcoal is loaded (known as charging) into the furnace from above. Smelting takes between 5-7 hours. During smelting most of the goethite content of iron ore is reduced to metallic iron. The iron bloom is formed from the reduced iron grains. The mine rubbish content of the ore and some iron oxides melts into slag. However, there is usually not enough room in the hearth for the slag, so it is important to tap out the molten slag regularly. At the end of the smelting process the breast-wall is broken out and the hot iron bloom is removed from the hearth and compressed using a wood-hammer.

2.4 Processing of the iron bloom

The iron bloom that is removed from the hearth becomes cold very fast so it must be re-heated in order to compress it repeatedly. During compression, the iron bloom looses its slag content and it then becomes dense. The iron bloom can only be forged if the slag content is low and its density high enough. Due to the spongy structure, it is very important to forge-weld the iron bloom. After forge-welding we end up with a homogenous, compact, good quality iron material. The forging also helps by refining the rough grain structure of the iron bloom. The Fig. 2 shows the steps of the early medieval iron manufacturing.

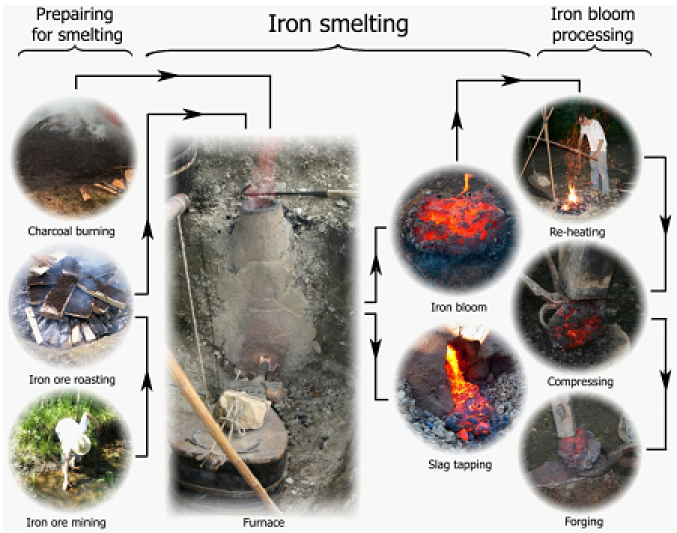


Fig. 2. The steps of the early medieval iron manufacturing.

3 Measurements and analysis

3.1 Temperature and gas-composition measurements

Temperature and gas-composition measurements were carried out during one of the smelting experiments to understand the physical-chemical and metallurgical processes of the bloomery. For the temperature measurements a Pt-PtRh thermocouple was used. There were four temperature measurement points on the front wall of the furnace: at upper, middle and lower levels of the stack and at a point in the hearth. The temperature measurement started when the first iron ore-charcoal mixture portion was added and stopped when the last portion was charged. In case of gas composition measurement about 5 liters of gas was sampled at the upper level of the stack (i.e. at the same point as the first temperature measurement). Later the gas sample was analyzed using gas chromatography. Fig. 3 shows the measurement points and the results of the measurements.

From these temperature measurement results we can say that the temperatures were fairly constant during the whole smelting experiment and the temperature in the hearth was high enough to obtain molten slag. From the gas composition measurement results we can say that the atmosphere of the furnace is reductive, it has high volume ratio of CO besides a relative low volume ratio of CO_2. The relative high H_2 volume ratio in the atmosphere can be explained by the wet-like charcoal charged into the furnace.

3.2 Technical analysis on iron ore and slag samples

Iron ore samples were examined by X-ray diffraction analysis and chemical analysis by ICP and XRF spectrometer. The Table. 1 shows the summarized results.

In general, the acid characteristic of the iron ore samples was established, as well as a high wt% of the goethite phase. The best iron ore was found in Petesmalom. Although, the iron ore from Petesmalom has the highest iron content, it contains too much phosphorus. However, its mine rubbish content is low, so a mixture of sand and wood ash has to be charged with the iron ore during the iron smelting in order to obtain enough slag. The Kék-Kálló valley iron ore mine rubbish content is too high, especially SiO_2. The high SiO_2 content indicates bad iron output because the SiO_2 bounds the FeO as fayalite ($2FeO \cdot SiO_2$) in the slag.The Fancsika iron ore has high iron content, but its quality is very inhomogeneous. Furthermore, its phosphorous content must also be high, because the iron bloom made from this ore was never forgeable. These iron blooms always had very high phosphorous content. The actual phosphorous content of the iron ore samples has not yet been established. The basicity of the Somogyszob iron ore is too high; it has a great deal of CaO content. Therefore, its slag has high viscosity at a lower iron smelting temperature. During the process of iron smelting the acid characteristic of the slag is advantageous, in that, the relative low metallurgical temperature (1100–1300°C; see Fig. 3) of the acid slag has a lower viscosity value then the basic slag and therefore easier to tap the acid slag out. Up until the time of writing only a few slag samples were examined using X-ray diffraction analysis and chemical analysis using ICP spectrometer. The Table .2 shows the summarized results.

Based on the results of X-ray diffraction analysis we can say that the slag samples always have some amorphous phase in addition to the crystallized fayalit phase. The high ratio of the amorphous phase is advantageous because its melting point is lower than that of the fayalit. We can raise the amount of the amorphous phase by adding wood ash with the iron ore during the iron smelting. The wood ash contains more or less Na_2O and K_2O which helps to form glassy phases with the SiO_2.From the results of the ICP spectrometry, the common characteristic of the tap slag is the high Fe concentration which is the main cause of the bad iron output.The slag has an acid characteristic; the silica content can bring about the forming of fayalite. The high CaO content does not come from the iron ore: the wood ash charged with the iron ore raised the base characteristics of the slag.

3.3 Technical analysis of iron bloom samples

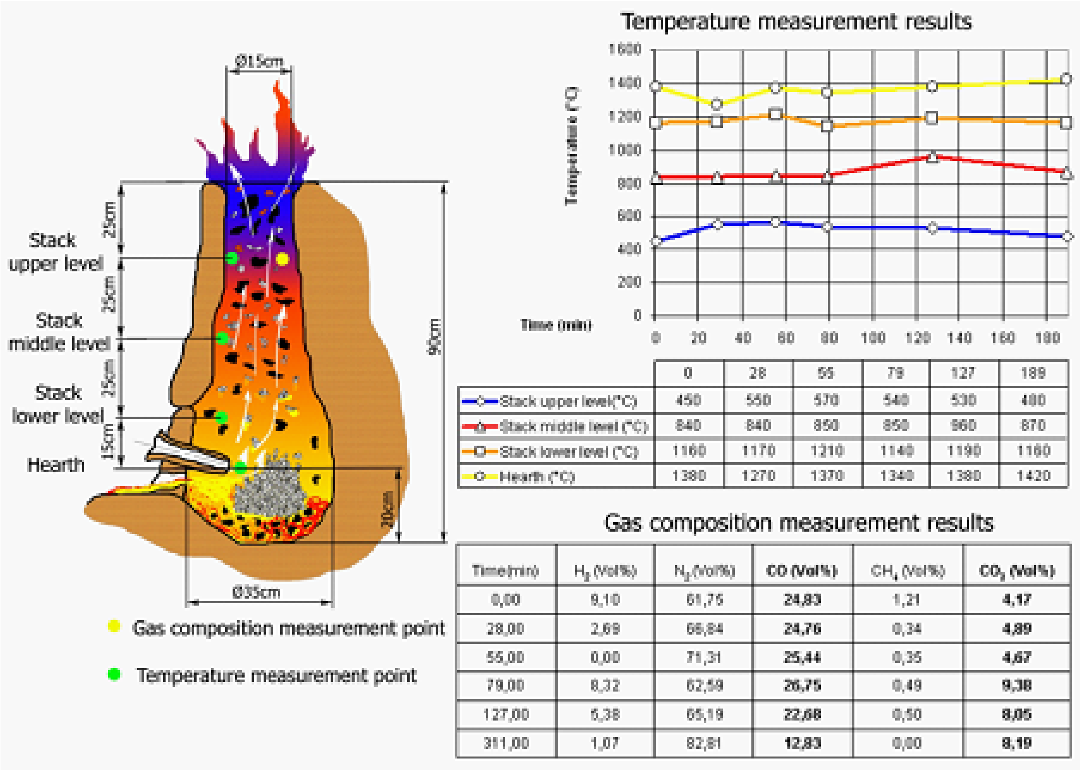
The iron blooms made from Fancsika iron ore were always very breakable during the forging and neither of them could actually be forged. Later, the iron blooms made from the Petesmalom iron ore were good for forging but, in a cold state, they proved to be very hard and brittle. Several metallographic analysis were carried out on iron bloom pieces. In addition to the metallographic analysis some iron bloom samples were examined by EDX spectrometry. On this way the reason of the embrittlement could be found. The Fig. 4a and Fig. 4b shows the metallographic picture of an iron bloom made from Fancsika and an iron bloom made from Petesmalom iron ore.

From the findings of the metallographic and EDX spectrometry analysis the common property of the samples examined has the low carbon content (we can see mainly ferrite grains on the metallographic pictures) and the slag inclusions. The high phosphorous content was also evident. In case of iron blooms made from Fancsika iron ore, much of the $Fe\text{-}Fe_3P$ eutectic appears on the metallographic picture. In the eutectic matrix we can see the ferrite grains with rounded contours.The melting point of the $Fe\text{-}Fe_3P$ eutectic is 1083°C [5]. The $Fe\text{-}Fe_3P$ eutectic usually melts with a forging temperature 1100–1300^{o}C, so is not possible to forge this material. The iron blooms made from Petesmalom iron ore has lower phosphorous content and there is much lower amount of $Fe\text{-}Fe_3P$ eutectic on the metallographic picture. However, the solute phosphorous content is very high in the ferrite grains; therefore the material is very hard and brittle in cold state. The phosphorous in the iron blooms comes from the iron ores. Modern agriculture uses many types of chemical fertilizers which can cause the phosphorous content of the iron ore lumps found nowadays. It would be interesting to know: If the ancient foundry men had any phosphorous problem in the early medieval times, Endre Zoltay carried out some chemical analysis on early medieval iron tools and weapons [3]. The results of the analysis revealed that the average phosphorous content in case of some iron product was 0,2–0,5. This high phosphorous content could cause embrittlement as well.

4 The metallurgy of the Bloomery

Based on the temperature and gas composition measurements and the technical analysis of iron ore, slag and iron bloom samples we were able to discover the possible metallurgical processes of the bloomery. During the roasting, the iron ore lumps lose their hydrate water content: the goethite becomes hematite:

$$2FeO(OH) \rightarrow Fe_2O_3 + H_2O \quad (1)$$



	0	28	55	79	127	189
Stack upper level(°C)	450	550	570	540	530	480
Stack middle level (°C)	840	840	850	850	960	870
Stack lower level (°C)	1160	1170	1210	1140	1190	1160
Hearth (°C)	1380	1270	1370	1340	1380	1420

Time(min)	H_2 (Vol%)	N_2 (Vol%)	**CO (Vol%)**	CH_4 (Vol%)	**CO_2 (Vol%)**
0,00	9,10	61,76	**24,83**	1,21	**4,17**
28,00	2,69	66,84	**24,76**	0,34	**4,89**
55,00	0,00	71,31	**25,44**	0,35	**4,67**
79,00	8,32	62,59	**26,75**	0,49	**9,38**
127,00	5,38	65,19	**22,68**	0,50	**8,05**
311,00	1,07	82,81	**12,83**	0,00	**8,19**

Fig. 3. Temperature and gas composition measurement points in the furnace and the results.

In case of good conditions the pre-reduction can occur during the roasting: a small amount of magnetite appears. The reducing agent is the CO:

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \tag{2}$$

So we charge dehydrated, pre-reduced iron ore lumps into the furnace which is filled up with charcoal. The portion of iron ore-charcoal mixture comes down from the throat to the hearth. This method can take over an hour. Let us examine a portion as it travels from the throat to the hearth! The air blast coming from the bellows contains O_2. The carbon of the charcoal burns in the air blast in front of the twyer, on this way CO_2 is formed:

$$C + O_2 \rightarrow CO_2 \tag{3}$$

The stability of the CO_2 is a function of temperature: there is an inverse proportionality between the temperature and the CO_2 content of the furnace atmosphere. Over 1000^{o}C there is no CO_2in the gas mixture. Due to the high temperature (1200–1300^{o}C, see Fig. 3) the CO_2 is not stable in the hearth; it forms CO according to Boudouard-reaction [6]:

$$CO_2 + C \rightarrow 2CO \tag{4}$$

This is the reason of the high CO concentration of the furnace atmosphere (20-25vol%, see Fig. 3). In the throat and in the upper part of the stack the pre-reduction goes on: the rest of the hematite is reduced to magnetite at a temperature of 500^{o}C. The reducing agent is still the CO:

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \tag{5}$$

Due to the large surface-area-to-volume-ratio of the porous iron ore the reaction surface of the indirect reduction is large. The portion comes down to the middle side of the stack where the temperature is higher, about 800^{o}C. At this temperature both the CO and the C can be the reducing agent, and there is the possibility of indirect and direct reduction. Indirect reduction:

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2FeO + CO \rightarrow Fe + CO_2 \tag{6}$$

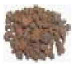
In case of direct reduction the transmitter agent is the CO, because only the CO can reach the reaction surface, but the solid carbon can not reach it [6]. So both the indirect and direct reduction is a gas-solid reaction. After indirect reduction the CO_2 obtained is partially unstable at a temperature of 800°C, so it reacts with the carbon according to Boudouard-reaction. From the summarized reaction of the indirect and Boudouard-reaction, the direct reduction is:

$$\begin{aligned} Fe_3O_4 + CO &\rightarrow 3FeO + CO_2 \\ CO_2 + C &\rightarrow 2CO \\ Fe_3O_4 + C &\rightarrow 3FeO + CO \end{aligned} \tag{7}$$

$$\begin{aligned} FeO + CO &\rightarrow Fe + CO_2 \\ CO_2 + C &\rightarrow 2CO \\ FeO + C &\rightarrow Fe + CO \end{aligned} \tag{8}$$

In this way metallic iron appears.The portion comes down to the lower part of the stack where the temperature is about

Tab. 1. Summarized chemical compositions of the examined iron ore samples.

Sample	Image	Chemical components (wt%)						ΣFe
		Fe_2O_3	SiO_2	CaO	Al_2O_3	P_2O_5	H_2O	
iron ore from Kék-Kállón valley		42..54	28..30	0	0	-	5..6	29..38
iron ore from Fancsika		27..67	17..60	0..5	5..6	-	4..9	19..47
iron ore from Somogyszob		46..61	14..32	6..17	3..8	3	6..8	32..43
iron ore from Petesmalom		80..82	3..5	0..3	0..1	7	9..11	56..58

Tab. 2. Summarized phase and chemical compositions of the examined slag samples.

Sample	Image	Phase (wt%)	components		Chemical components (wt%)					
		Fayl	Quar	Glass	SiO_2	CaO	MgO	FeO	MnO	Al_2O_3
Slag from fancsika ore		10..20	0..5	75..90	22..32	10..12	1	26..32	2..3	2..3
Slag from Petesmalom ore		0..50	10..15	30..85	45	11	1	24	3	3

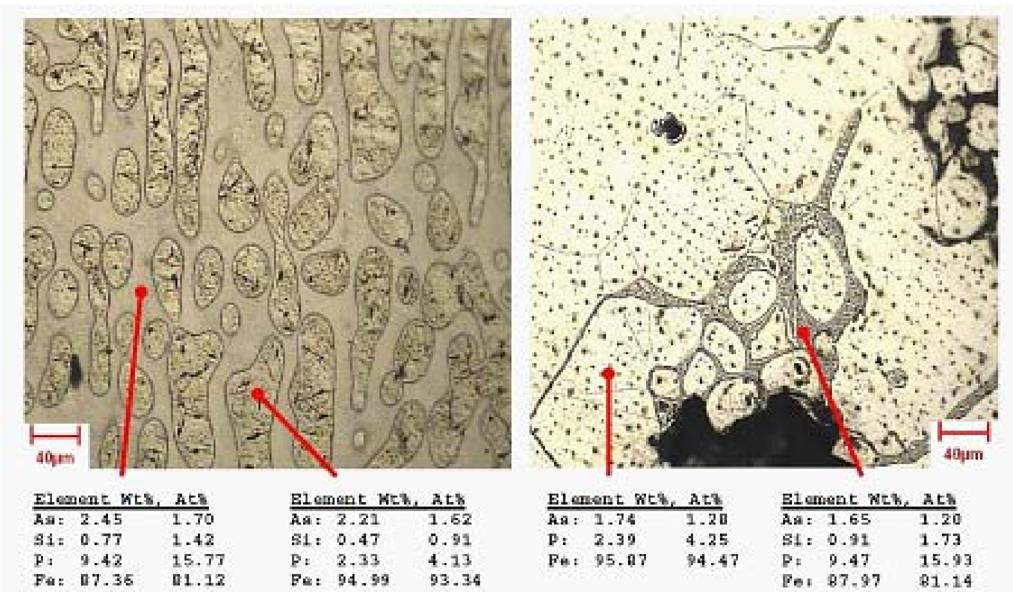


Fig. 4. Metallographic picture of iron bloom samples (200x). a. iron bloom made of Fancsika iron ore b. iron bloom made of Petesmalom iron ore.

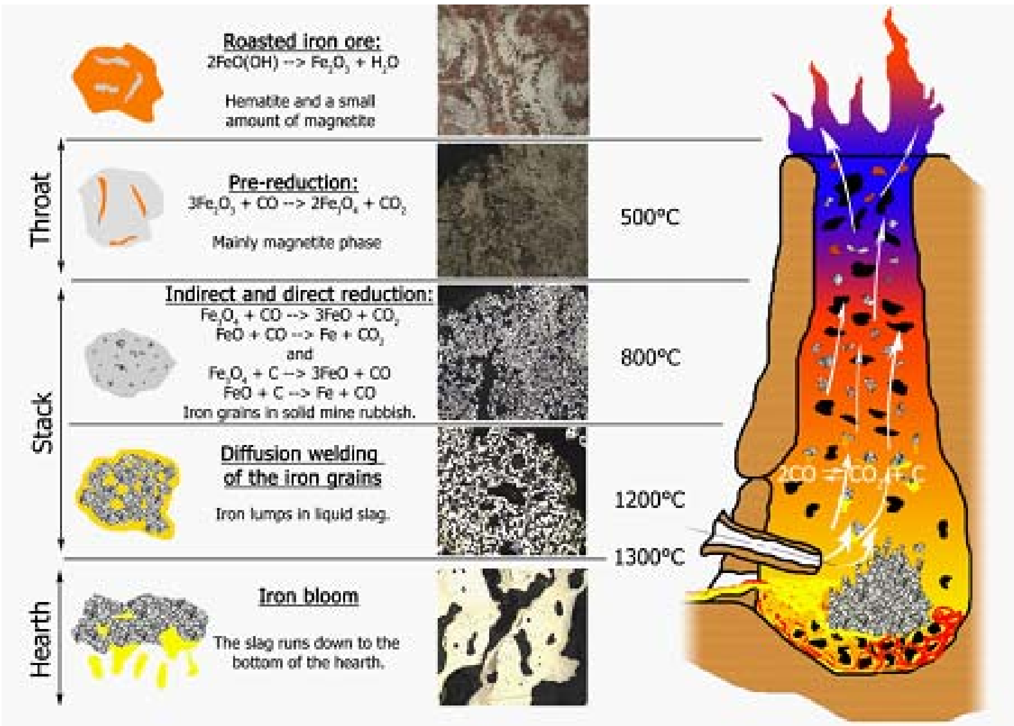


Fig. 5. The metallurgy of the bloomery.

1200^{o}C. At this temperature the mine rubbish of the iron ore melts into slag. The reduced iron grains do not smelt but they can get close to each other to weld together (diffusion welding in liquid slag). The viscosity of the slag is lower, the higher the temperature is, therefore the conditions of diffusion welding are better in the hearth.The iron bloom can be obtained in this way. The liquid slag protects the surfaces of the iron bloom from the re-oxidation in front of the twyer and it also helps later during the re-heating and forge-welding.

The Fig. 5 shows the metallurgy of the bloomery. Some smelting experiment models were carried out under laboratorial conditions. In the middle of the Fig. 5 small metallographic pictures show the state of the iron ore based on the experiment models.

5 Summary

Several smelting experiments were carried out to find out how the iron was made in the early medieval times. The experiments performed are considered to provide true representations of the period iron smelting technologies.Dense iron blooms, good for forging, were obtained, but, on occasions, they were found to be breakable during processing or they were brittle in cold state. Based on the findings of the metallographic and EDX spectrometry analysis of iron bloom samples, the reason of the embrittlement is the high phosphorous content. We can still find good quality iron ore lumps in Hungary. From the X-ray diffraction and chemical analysis of the iron ore we can state that their porous structure ensures large reaction surface for the fast reduction. In addition, the phosphorous content of the iron blooms comes from the iron ores. Due to the acid characteristic of the iron ores the obtained slag has low viscosity at the metallurgical temperature of the iron smelting.Furthermore, it is possible to decrease the melting point of the slag by adding some wood ash with the iron ore in the furnace.During the smelting experiments temperature and gas composition measurements were carried out.The results showed that the metallurgical temperature of the furnace is high enough and the atmosphere of the furnace has high enough concentrations of CO to acquire metallic iron in the stack.The gas-solid reactions have the main role in the formation of metallic iron grains in the stack. The iron grains weld together in the liquid slag in the hearth, and forms the iron bloom.

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