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METALLURGICAL PROCESS IN ANCIENT SHAFT FURNACE - THEORETICAL CONSIDERATIONS

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ABSTRACT

The latest knowledge from theoretical fundamentals of metallurgy makes new possibilities for reconstruction of ancient ironmasters work. It is especially refer of computer thermodynamic data bases using. The theoretical metallurgical fundamentals of iron compounds reduction process and thermal issues connected with it are presented in the treatise. The results of these deliberations could provide projection of shaft furnace constructional parameters as well as the technological parameters of reduction process.

Course of metallurgical process in ancient shaft furnace could be presented in a simplified way as a chemical reactor. Streams of entrances materials in reactor are iron ore, charcoal and air. Exit products are: sponge iron, slag and gases. All those materials were characterized from chemical point of view and implemented role in a process.

During the smelting process in shaft furnace, the charcoal combustion process can be marked. It produces heat to bring the temperature inside the bloomery and the carbon monoxide which is needed to reduction of iron ore. For this chemical reactor the mathematical model were elaborated on the base of latest thermodynamic data. In this model a scheme of reduction reaction in higher and lower temperatures has been marked out. From the elaborated materials balance it is able determining a quantitative of each material takes part in smelting process.

Key words: ancient shaft furnace, metallurgical process, material balance

1. INTRODUCTION

State-of-the-art knowledge in metallurgy, including computer thermodynamic databases, affords new possibilities of understanding and reconstructing the work of ancient metallurgists. This paper presents the theoretical assumptions underlying the metallurgy of the process of reduction of iron compounds as well as the related thermal issues. The ideas presented below may help us understand the working parameters of the ancient shaft furnace, which can help us reconstruct the design and metallurgical process.

2. ANCIENT SHAFT FURNACE MODEL

The course of the metallurgical process in an ancient shaft furnace may be presented in a simplified and schematic way by means of a graphical model. Figure 1 presents such a model in the form of a chemical reaction flow chart, which disregards the shape and design of the furnace and its metallurgical parameters. Modern scientific language describes such means of process presentation as the chemical reactor.

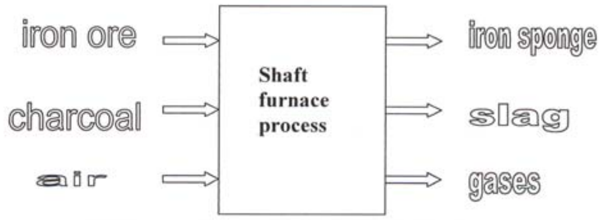

Figure 1 - Ancient ironmaking process model

Assuming that the process takes place within an enclosed space, i.e. in a chemical reactor, the following materials are supplied to the furnace:

- iron ore,
- charcoal,
- air.

Iron ore is a natural mineral rich in iron compounds. There is a variety of iron ores, composed of various chemical compounds and containing various levels of iron, other chemical compounds, e.g. silicates, Al_2O_3, CaO, etc., and water. We may assume here, however, that iron ore is composed primarily of Fe_2O_3 and SiO_2; the other components may be disregarded due to their low concentrations and the fact that most of them get oxidized in previous process of ore roasting.

Charcoal is produced as a result of the so-called dry distillation of wood. Charcoal is characterized by a high concentration of carbon and considerable porosity, i.e. well-developed external surface. It can be assumed that charcoal is composed of pure carbon, as the concentrations of the other components are low and they may be disregarded here. One has to remember that ancient metallurgists used fresh-cut wood in the metallurgical process. Although “fresh” wood contains a high level of moisture, it undergoes distillation during the metallurgical process, releasing high amounts of gases taking part in the reduction.

Air contains around 21% of oxygen and 79% of nitrogen and is a primary source of the oxygen required for carbon combustion, for the oxidation of heat-releasing chemical reaction used to obtain suitable temperature and the production of carbon monoxide.

Even though the schematic model does not show it, also sand could be used during the ancient metallurgical process. The metallurgical slag blocks found during archaeological excavations contain fayalite, which contains around 30 per cent of silica per unit of weight. Some iron ores contain lower concentrations of silica. Therefore it may be concluded that sand was used as a silica carrier for the reaction.

As can be seen in Figure 1 the ancient ironmaking process yielded the following end products:

- iron sponge,
- metallurgical slag,
- gases.

Iron sponge is the most important product of the ancient metallurgical process. From the chemical point of view, it is a kind of iron alloy which contains also other chemical elements. It can be assumed that the iron contained at least 96 – 99%. The other components included coal, manganese, silicon, phosphorus, sulphur. It is hard to determine precisely the chemical composition of iron sponge. Iron sponges are not normally found during archaeological excavations, as they were used as a valuable material for the manufacturing of various useful objects. The objects were most probably produced through multiple forging of the iron sponge.

Metallurgical slag is a by-product of the ancient metallurgical process and the only product of the metallurgists' work remaining until modern times. The slag blocks found during archeological excavations have been thoroughly examined by scientists. They vary in terms of size, shape and chemical composition. These characteristics are usually determined by the place of their origin, i.e. the design of the furnace and the chemical composition of the iron ore used. However, the most important component of the slag, in particular in the area of the Swietokrzyskie Mountains, is the so-called fayalite, i.e. a mineral compound composed of two oxides: iron monoxide and silicon dioxide; chemically: $2 \cdot FeO \cdot SiO_2$. Fayalite contains around 70% of iron monoxide and around 30% of silica. The melting point of fayalite is 1170 – 1200 ^oC (depending on the other admixtures).

Gases – Also gases are produced during the metallurgical reduction process. We may speculate as to their composition. They contained nitrogen, CO, CO_2 and most probably also gaseous oxygen.

Two processes may be distinguished during the ancient metallurgical process:

- charcoal burning; which produces heat for the process and releases CO required for the reduction,
- reduction of iron oxides; charcoal or CO may be used as the reducing agents; the products include metallic iron and slag (reduction usually requires heat).

Combustion of carbon in oxygen may proceed in two ways, depending on the so-called oxygen surplus. With sufficient supply of oxygen carbon is burnt completely; the product is CO_2:

- *Complete combustion*

$$C + O_2 = CO_2 \qquad (1)$$

The reaction is exothermic, and it releases approx. 394 kJ/mol of heat (at the temperature of 1200 ^oC). With insufficient supply of oxygen the combustion process first produces CO, and then possibly CO burns to form CO_2.

- i*ncomplete combustion:*

$$2\,C + O_2 = 2\,CO \qquad (2)$$

CO oxidation

$$2\,CO + O_2 = 2\,CO_2 \qquad (3)$$

Both of the reactions are exothermic, and they release approx. 110.5 kJ/mol and 283.5 kJ/mol of heat respectively (at the temperature of 1200 ^oC). Reactions (1) and (2) are irreversible, which means that they "proceed to the right" and cause carbon oxidation. Reaction (3) is also irreversible at lower temperatures (up to 1500 ^oC), but it becomes reversible at higher temperatures, whereby CO_2 is reduced to CO and then to oxygen.

In the carbon–oxygen system, CO_2 may react with carbon, which is referred to as the Boudouard reaction:

$$C + CO_2 = 2\,CO \qquad (4)$$

The reaction is reversible, i.e. it proceeds in both directions, depending on the conditions. For temperatures below 400 ^oC it proceeds "to the left", i.e. CO is decomposed to give off carbon and CO_2; such reactions are referred to as exothermic reactions, in which the amount of heat produced depends on the temperature. For temperatures exceeding 1000 ^oC the reaction proceeds "to the right", i.e. CO is produced; such reactions are called endothermic reactions, in which the amount of heat absorbed depends to a large extent on the temperature. With temperatures below 400 and above 1000^o C the course of the reaction does not depend on the composition of the gaseous atmosphere. On the other hand, with temperatures ranging between 400 and 1000^o C the course of the reaction depends on the composition of the gaseous atmosphere. For lower temperatures, even with low CO levels, the reaction proceeds "to the right", and heat is released. As the temperature increases more CO in the gaseous atmosphere is required for the reaction to proceed.

The goal of the reduction process, not only in ancient metallurgy, is to create conditions for "the absorption" of oxygen from oxides. This requires reduction atmosphere to be formed. In the case of iron oxides, the best reducing agents are gases, for the metallurgical process - CO. Other reducing agents, e.g. hydrogen, were most probably of little importance for ancient metallurgical process, as their level in ancient blast furnaces was low. The chemical reactions proceed in the places of direct contact between the reacting substances. With gaseous reducing agents the contact surface is relatively big, because each piece of the ore is surrounded by the reducing gas. Although solid coal can also be used as the reducing agent, it requires increased temperature, and the small contact surface of coal pieces with the ore indicates that this kind of reduction in the ancient metallurgical process was of little importance (T. Mazanek, 1969).

An ancient furnace contained a large amount of fayalite, i.e. a compound of iron monoxide and silicone dioxide. Figure 2 presents the particular phases in the function of temperature in an equilibrium system of these two oxides.

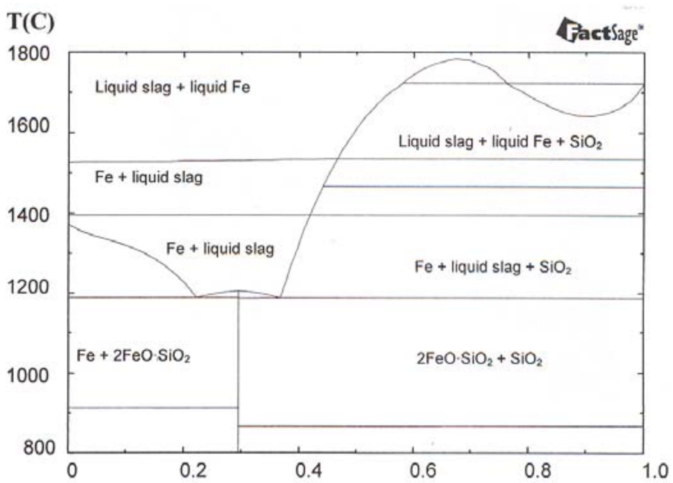

Figure 2 - Equilibrium FeO – SiO_2 system in the temperature function (FactSage, 2004)

The diagram shows the phases that exist in the system in the function of temperature. The axis of abscissae shows FeO and SiO_2 levels. The values on the left ("0") represent FeO exclusively, while those on the right ("1") represent SiO_2. The values in between represent the changing concentrations of both oxides, assuming that their sum is 1. As can be seen from the diagram, with the level of SiO_2 between 0.2 and 0.4 and the temperature of approx. 1200 ^oC, the system produces liquid fayalite and metallic iron. After the temperature is lowered, fayalite changes its state from liquid into solid and the reaction yields solid metallic iron or silica, depending on the concentration of both oxides. For higher levels of silicone dioxide the reduction of the iron oxides requires much higher temperatures, and once the concentration of 0.6 is exceeded, the reaction stops. With lover levels of silicone dioxide, the reduction of iron oxides is possible, but it requires higher temperatures. Metallic iron in the liquid state is formed at temperatures exceeding 1540 ^oC. A precise thermodynamic analysis shows that the reduction of iron from fayalite in an ancient shaft furnace is very unlikely.

The analysis of the reduction of iron oxides by means of carbon monoxide in an ancient furnace may be based on the so-called Fe-O-C equilibrium system. Figure 3 presents a diagram showing the reduction.

The diagram shows the possible chemical reactions involving iron oxide reduction, depending on the temperature and composition of the reduction atmosphere. It has been assumed that the reduction atmosphere in this system consists merely of carbon monoxide and dioxide; the axis of ordinates represents the quotient of CO partial pressure and the sum of CO + CO_2. Assuming that the iron ore used in an ancient shaft furnace contained Fe_2O_3, the reduction of this oxide may proceed in two ways, depending on the temperature. The threshold temperature is 572 ^oC.

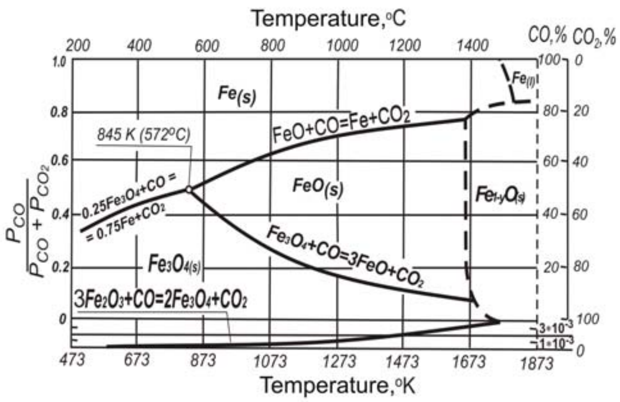

Figure 3 - The remaining conditions for the above reactions to take place

For temperatures below 572 ^oC Fe_2O_3 is reduced by CO to Fe_3O_4, which is an oxide containing less oxygen bound with iron. Subsequently, Fe_3O_4 is reduced to metallic iron. In view of the temperature, the reaction is referred to as reduction in the solid state. The reactions are represented by the following equations:

$$3\,Fe_2O_3 + CO = 2\,Fe_3O_4 + CO_2 \quad (5)$$

$$Fe_3O_4 + 4\,CO = 3\,Fe + 4\,CO_2 \quad (6)$$

Both reactions are endothermic, i.e. they require approx. 34.4 kJ/mol and approx. 3.9 kJ/mol of heat respectively (in terms of temperature = 1200 ^oC).

For temperatures exceeding 572 ^oC, Fe_2O_3 is also reduced to Fe_3O_4 by CO, but Fe_3O_4 is reduced to FeO, and not like before to metallic Fe. It is only FeO that can be reduced to metallic iron. This can be expressed by the following equations:

$$3\,Fe_2O_3 + CO = 2\,Fe_3O_4 + CO_2 \quad (7)$$

$$Fe_3O_4 + CO = 3\,FeO + CO_2 \quad (8)$$

$$FeO + CO = Fe + CO_2 \quad (9)$$

Reactions (7) and (9) are endothermic, i.e. they require approx. 34.4 kJ/mol and 18.6 kJ/mol of heat respectively. On the other hand, reaction (8) is exothermic and gives off around 40.4 kJ/mol of heat (in terms of temperature = 1200 ^oC).

Figure 3 also presents the remaining conditions which have to occur for the above reactions to take place. Apart from the temperature, also the gaseous atmosphere of the iron oxide is important. The axis of ordinates represents the ratio of CO to the sum of CO + CO_2 (it is assumed here that the system involves only these two gases, and their sum amounts to 100 %). The solid lines represent the state of equilibrium of the reaction indicated above them. The areas between the lines indicate the state of stability of a given compound or iron. For example, the area described as “I” indicates the stability area for Fe_3O_4. As can be seen in the diagram, metallic iron can exist only with a high (over 80%) content of CO in the CO + CO2 mixture. On the other hand, Fe_2O_3 may be produced only with very low CO content.

How to use the diagram to explain the reduction processes in an ancient shaft furnace? Let us assume that we place Fe_2O_3 in a gaseous atmosphere at the temperature of 1200 ^oC, with no CO present. Then, we increase the CO content in the mixture of gases. We will notice that already with a minimum content of CO, reduction to Fe_3O_4 will begin. With the CO level at 12% the reduction to FeO will start. However, the reduction to metallic iron will begin only with the CO level of 70 %. In temperatures lower than 572 ^oC, reduction directly from Fe_3O_4 to metallic iron will be observed, with a relatively low level of CO, at approx. 40 %.

The diagram shows the so-called thermodynamic conditions, and disregards the duration. As can be seen from the diagram, although thermodynamically Fe_2O_3 reduction in the temperature lower than 400 ^oC is possible, in a simpler way, directly to metallic iron, but the analysis does not take into account the duration of the reaction. The duration of the process depends on the temperature. For example reduction in the temperature of 400 ^oC would have to last several dozen years. This is indicated by the calculations, as it is hard to verify it by experimental methods. Only temperatures of 800 – 1000 ^oC can bring down the reduction time to approx. a dozen or several dozen minutes, i.e. real time for practical application.

3. THE MATERIAL BALANCE IN THE ANCIENT SHAFT FURNACE PROCESS

The deliberations presented above do not allow for a quantitative analysis of the possible chemical reactions. The quantitative relations may be determined through a balance of the materials which take part in the reactions. The calculations of the balance figures require the atomic weights of the elements involved. It is assumed that the atomic weight of iron is 56 g, oxygen 16 g, carbon 12 g. The molecular weights of the compounds involved are as follows: Fe_2O_3 – 160 g, Fe_3O_4 – 232 g, FeO – 72 g, CO – 28 g, CO_2 – 44 g.

For Fe_2O_3 reduction in low temperatures, for the stoichiometric equations of reactions (5) and (6), the following results were obtained:

I. For reaction (5):

3 x 160 g of Fe_2O_3 reacts with 28 g of CO and yields 2 x 232 g of Fe_3O_4 and 44 g of CO_2.

in terms of kilograms:

- the reduction of 1 kg of Fe_2O_3 requires 0.0583 kg of CO,
- the reaction yields 0.967 kg of Fe_3O_4 and 0.0917 kg of CO_2.

II. For reaction (6):

232 g of Fe_3O_4 reacts with 4 x 28 g of CO and yields 3 x 56 g of Fe and 4 x 44 g of CO_2.

in terms of kilograms:

- the reduction of 1 kg of Fe_3O_4 requires 0.483 kg of CO,
- the reaction yields 0.724 kg of Fe and 0.759 kg of CO_2

The reduction of 0.967 kg of Fe_3O_4 requires 0.467 kg of CO; the reaction yields 0.700 kg of Fe and 0.734 kg of CO_2.

To sum up, the reduction of 1 kg of Fe_2O_3 requires 0.525 kg of CO; the reaction yields 0.700 kg of Fe and 0.825 kg of CO_2. Assuming that 1 kg of ore contains around 50 – 60% of Fe_2O_3, the reduction requires 0.289 kg of CO. The reaction yields 0.385 kg of Fe and 0.454 kg of CO_2. Assuming that 1 mole of CO contains 12 g of carbon and 16 g of oxygen, then 0.289 kg of CO contains 0.124 kg of carbon and 0.165 kg of oxygen.

To sum up: the reduction of 1 kg of ore, for reactions (5) and (6), with the Fe_2O_3 content of 55 %, requires 0.124 kg of carbon and 0.165 kg of oxygen; the reduction reaction yields 0.385 kg of iron and 0.454 kg of CO_2.

The reduction of Fe_2O_3 in higher temperatures, for reactions (7), (8) and (9), yields:

I. For reaction (7) the same amounts as those yielded in reaction (5).

II. For reaction (8):

232 g of Fe_3O_4 reacts with 28 g of CO and yields 3 72 g of FeO and 44 g of CO_2

In terms of kilograms:

- the reduction of 1 kg Fe_3O_4 requires 0.121 kg of CO,
- the reaction yields 0.931 kg of FeO and 0.190 kg of CO_2

The reduction of 0.967 kg of Fe_3O_4 requires 0.117 kg of CO; the reaction yields 0.900 kg of FeO and 0.184 kg of CO_2.

III. For reaction (9):

72 g of FeO reacts with 28 g of CO and yields 56 g of Fe and 44 g of CO_2

in terms of kilograms:

- the reduction of 1 kg of FeO requires 0.389 kg of CO,
- the reaction yields 0.778 kg of Fe and 0.611 kg of CO_2

The reduction of 0.900 kg of FeO requires 0.350 kg of CO; the reaction yields 0.700 kg of Fe and 0.550 kg of CO_2.

To sum up, the reduction of 1 kg of Fe_2O_3 requires 0.954 kg of CO; the reaction yields 0.700 kg of Fe and 1.493 kg of CO_2. Assuming that 1 kg of ore contains approx. 50 – 60% of Fe_2O_3, the reaction requires 0.525 kg of CO. The reaction yields 0.385 kg of Fe and 0.821 kg of CO_2. Assuming that one mole of CO contains 12 g of carbon and 16 g of oxygen, then 0.525 kg of CO contains 0.225 kg of carbon and 0.300 kg of oxygen.

To sum up: the reduction of 1 kg of ore, for reactions (7), (8) and (9), with the Fe_2O_3 content of 55 %, requires 0.225 kg of carbon and 0.300 kg of oxygen; the reduction yields 0.385 kg of iron and 0.821 kg of CO_2.

The oxygen required for the reduction processes comes from the air blown into the furnace, which consists of nitrogen and oxygen. Hence also nitrogen will be present in an ancient shaft furnace, even though it will not take part in the chemical reactions. As the air contains 21% of oxygen, the level of nitrogen will be as follows:

- for lower temperature reactions 0.620 kg,
- for higher temperature reactions 1.129 kg.

The weight balance calculations presented above refer to reduction reactions in stoichiometric, i.e. theoretical conditions. How to calculate the yield, i.e. the amount of iron which could be obtained in actual conditions? Knowing the chemical composition of a given type of ore used for a specific melt, we can determine it easily. We know it from the chemical composition of the slag and its weight; the same data will allow us to estimate the weight of the chemical compounds contained in it, i.e. FeO, SiO_2, etc. With a large dose of certainty, we can assume that silica is not reduced during the process, i.e. the same amount of SiO_2 as that loaded into the furnace together with the ore can be found in the slag block. Knowing the chemical composition of the ore used, one can calculate its mass. However, we do not know whether the iron ores found today - which vary to a large extent in terms of their chemical composition (depending on the place of origin) - were used in ancient times. Besides the slag blocks found these days also vary in terms of their chemical composition.

An attempt was made to estimate the yield of metallic iron using ancient production methods. The estimates were based on calculations using data on chemical composition of the iron ore and slag blocks coming from the area of the Swietokrzyskie Mountains (Bielenin, 1992). The average levels of iron oxides and silicone dioxide adopted for the calculations are as follows:

- iron ore: Fe_2O_3 50 – 60 %; SiO_2 15 – 20 %,
- slag block: FeO 50 – 60 %; SiO_2 20 – 30 %.

The calculations refer to a 1-kg slag block. The SiO_2 content in the block is 200 – 300 g. Assuming that the silicone dioxide is not reduced, its content in the slag block should remain the same. Therefore the weight of ore containing 200 – 300 g of silicone dioxide (15–20%) is 1333 – 1500 g. Following this train of though, to produce a slag block of 1 kg, 1.333 – 1.5 kg of iron ore had to be used.

1333 g of ore, with the Fe_2O_3 content at 50%, contains 466 g of iron, whereas a slag block of 1000 g, with the FeO content at 50 %, contains 389 g of iron. The difference in the content of iron in the ore and the block in this case amounts to 77 g (i.e. the yield of iron in an ancient shaft furnace should be 77 grams).

1500 g of ore, with the content of Fe_2O_3 at 60%, contains 630 g of iron, whereas 1000 g of a slag block, with the FeO content of 60 %, contains 467 g of iron. The difference in the content of iron in the ore and the block in this case amounts to 163 g (i.e. the yield of iron in an ancient shaft furnace should be 163 grams).

Summing up the calculations, it can be concluded that 1 kg of iron ore yields 58 – 109 g of metallic iron in an ancient shaft furnace.

4. SUMMARY

Based on the present-day theoretical knowledge related to the theory of metallurgical processes and the results of previous archaeological and metallurgical research of the process of obtaining "iron" in an ancient iron furnace, the process model has been developed, specifying the input and output materials fluxes. It has been assumed that the process proceeds in an enclosed space, i.e. in the so-called chemical reactor. The process involves the following supply materials: iron ore, charcoal, air. The process yields: iron ingot, slag block and gases.

The analysis of the process allowed for compiling a mass balance of the process. A list of the calculation results is presented in Table 1. The results presented in the table indicate that in order to produce a 1-kg slag block, 1.33 ÷ 1.50 kg of iron ore has to be used. The proportion of the charcoal to the ore is 1:1. The process required 7.6 kg of air, which amounts, in terms of volume at 20 ^{o}C, to 6.4 m^3. The process yielded 58 ÷ 109 g of iron and 8.9 kg of gas, including carbon monoxide and dioxide, nitrogen and oxygen. The volume of the gases at 1200 ^{o}C amounted to approx. 30 m^3.

The calculations presented are simplified and they are estimates. The calculations disregard the design parameters of the furnace and the technological parameters of the process. Developing a more precise model of the technological process of iron making in an ancient iron furnace requires further research, including laboratory tests.

Table 1 - Material balance of the ancient ironmaking process

Input			Output		
	Material	Mass, kg		Material	Mass, kg
1	Iron ore	1.33 ÷ 1.50	1	Metal	0.058 ÷ 0.109
2	Charcoal	1.33 ÷ 1.50	2	Slag	1.0
3	Air	7.618	3	Gases	8.914

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