SLAG IN THE PRODUCTION OF WROUGHT IRON

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ABSTRACT

Production of iron, steel, and various metals is in close relation with slags. Slag compositions and their metallurgical properties depend on the applied technological processes. In old times when reduction of iron ores resulted wrought iron that was produced at temperatures lower than the iron melting point, the slag had also important role like today in the modern steel industry.

Slag rich in iron oxide protected the reduced iron against carburization and also against oxidation. Liquid viscous slag that was collected in hearths of those simple metallurgical reactors had also role as a medium for transport of the first reduced iron. That first reduced metallic iron was similar to the iron sponge. Slag rich with wustite percolated among particles of charcoal towards the hearth and it protected iron against carburization.

Metallic iron and slag collected in the hearths of reduction reactors where single reduced iron »drops« welded or sintered, respectively, together into more or less homogeneous bulk. This welding or sintering of the reduced metallic iron took place in the viscous slag at about 1200°C. The not reduced slag flowed out of the reduction reactor.

In the reduction process, the metallic iron was formed as tiny rounded shaped particles being surrounded by slag rich in FeO on the surface of the ore lumps and in the pores. Initially slag was not liquid yet. In this stage, sintering of reduced iron particles started. As ore lumps with metallic iron descended into high-temperature regions, slag started to soften and melt. Viscous slag descended together with the reduced iron towards hearth.

Micrographs of single phases will illustrate the whole process from the initial formation of iron sponge to the flow of slag and reduced iron into the zone of sintering or welding, respectively, in the reactor hearth. Further, slag phase compositions that are formed in these processes will be presented too.

INTRODUCTION

Reduction of iron oxides with carbon, carbon monoxide and hydrogen is essential for the production of iron in blast furnaces. The products of iron ores reduction in the blast furnace are molten pig iron, liquid slag and blast furnace gases. Liquid pig iron is the basic alloy for steelmaking.

Modern direct reduction processes of high-grade iron ores or concentrates with hydrogen and carbon monoxide take place at temperatures that are below the melting points of iron and slag that are formed in standard processes. These processes take place between 800 and 1000°C. The products of reduction are solid.

In the direct processes in rotary furnaces using coal as reducing agent the temperatures may be higher but regularly below the sintering temperature of coal ash. Reduction products in these direct processes are mainly metallized pellets, briquettes or lumpy ore.

Direct reduction processes of production of wrought iron from iron ore have take place at about 1200°C. At those temperatures slag has to be liquid. The objective of our research was to describe mechanisms of wrought iron production.

METHODOLOGY

Two slag, primary and final, are formed during the reduction process in making pig iron. Primary slag is rich with FeO. Its composition can be presented by the $CaO–FeO-SiO_2$ ternary system [1]. Amount of FeO, the slag composition, and its basicity influence the melting point of primary slag. Final slag is mainly composed of CaO, MgO, SiO_2 and Al_2O_3. Their contents represent 85 to 96% of the total mass. Depending on the composition of used ores, the slag can contain also MnO and other oxides that come into the blast furnace with the burden. Slag contains also desulphurization products, such as calcium and magnesium sulphide. The slag composition can be represented by the CaO – MgO – SiO_2 – Al_2O_3 quaternary system at 10 to 15% Al_2O_3 [1]. Phase composition of blast-furnace slag consists of melilith (akermanite – $2CaO^{\cdot}SiO_2^{\cdot}2MgO$ and gehlenite – $2CaO^{\cdot}SiO_2^{\cdot}Al_2O_3$) monticellite – $CaO^{\cdot}MgO^{\cdot}SiO_2$, merwinite – $3CaO.MgO^{\cdot}2SiO_2$, dicalcium silicate $2CaO^{\cdot}SiO_2$, forsterite – $2MgO^{\cdot}SiO_2$, spinell $MgO^{\cdot}Al_2O_3$, diopside $CaO^{\cdot}MgO^{\cdot}SiO_2$.

In the past, the ironmaking process in bloomery furnaces actually represented direct method of iron ores reduction. The product of reduction was wrought iron that could be forged into various products in forges and smitheries.

Production in these simple metallurgical set-ups took place in various regions in the world. Remnants of slag reveal places where wrought iron was produced and then worked into variety of products. Numerous archeological finds revealed pieces of various tools, ornaments and weapons, such as swords, daggers, and knives.

Temperatures in those metallurgical furnaces did not regularly exceed 1250°C. Iron that was collected in the bloomery furnace hearths was not liquid but semisolid. Only slag was liquid and it drained off the furnace during the reduction process. Shapes of slag samples indicated that the slag was sluggish due to its high viscosity.

The main components found in the slag were FeO and SiO_2. Their amounts varied from 48 to 65 mass% FeO, and 26 to 33 mass% SiO_2. Other oxides, such as Al_2O_3, CaO, MgO, were present in smaller amounts. MnO content varied in a wider range, from 5 to 15 mass%, depending on the content of manganese oxide in the ore. Also alkalis, mainly K_2O, can be found in slag. According to FeO and SiO_2 contents, fayalite, $2FeO^{\cdot}SiO_2$, is the most abundant in the primary slag. Fayalite can contain also various amounts of CaO, MnO, and also MgO.

Figure 1 represents the microstructure of a slag from the 3rd century AD. This slag is composed of wustite, FeO, fayalite, $2(FeO,CaO).SiO_2$, and potassium aluminosilicate.

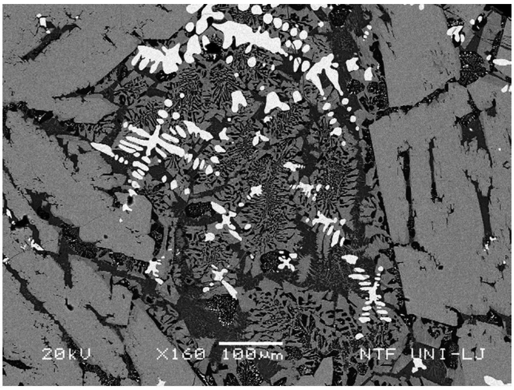

Figure 1: Composition of slag, containing wustite, fayalite, and potassium aluminosilicate

The main products of the bloomery process were liquid slag and iron that was found in the bloomery furnace hearth. Since temperatures of those processes were only around 1250°C, the reduced iron did not melt. In the description of those processes there is mentioned gradual agglomeration of reduced iron in the furnace hearth, or welded iron as product, respectively [2, 3, 4, 5, 6].

Heat that was liberated in the combustion zone was sufficient that fayalite slag was liquefied and drained out of the furnace. This is the indication that there existed conditions for the reduction of iron ore to metallic iron, and for the formation of slag. Thus conditions for the agglomeration of granules of reduced iron were created by the sintering process in the bloomery furnace hearth. The process of iron ore reduction was intentionally controlled by metallurgists in such a way that one part of ore was reduced to metallic iron while the rest FeO reacted with SiO_2 to form fayalite with the melting point of 1205°C. Addition of calcium oxides extended the region of molten slag. Figure 2 represents the region of molten slag in the CaO – FeO – SiO_2 system, that exists around the $2CaO{\cdot}SiO_2$ – $2FeO{\cdot}SiO_2$ tie line in that system.

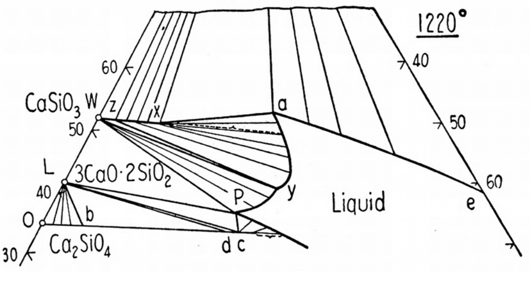

Figure 2: Phase relations in the CaO – FeO – SiO_2 system at 1220°C [7]

RESULTS AND DISCUSSION

In direct reduction processes iron ores were reduced with carbon of charcoal and with carbon monoxide that was formed by the gasification of charcoal.

Iron ore was reduced with wood charcoal at 1150°C. From reduced iron ore samples for metallographic investigations were manufactured.

In reduction of iron ores, metallic iron is formed at first on the exterior of single ore grains and in the grain pores. Figure 3 shows the metallic iron on the exterior surface of iron ore pieces, and the phase boundaries after the process of metallization was completed. Crystals of metallic iron are growing and this represents the beginning of formation of iron sponge.

On the surface or in the pores of ore grains also a continuous homogeneous layer of metallic iron is formed that grow with the agglomeration of single globules.

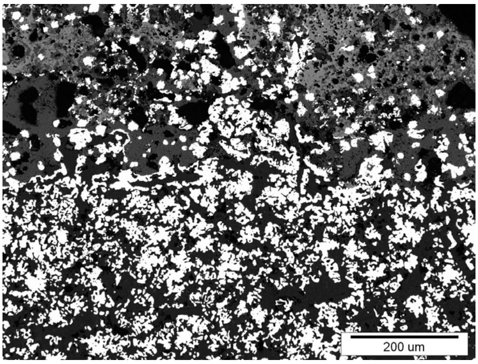

Figure 3: Process of metallization at the beginning of formation of iron sponge

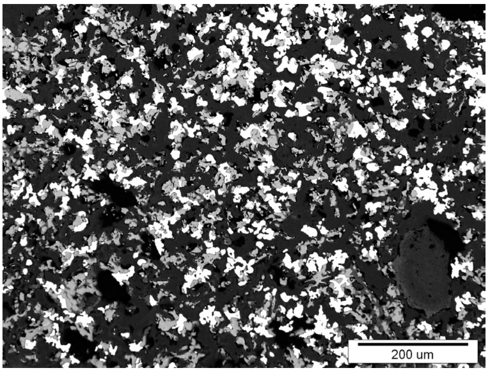

Figure 4: Single grains of metallic iron enveloped with slag

Slag was formed also between single grains of metallic iron and iron oxides that were after the reduction to metallic iron enveloped with slag that protected them against carburization (Figure 4).

In present steelmaking processes slag is important, still greater importance it had in the bloomery processes since it had to protect the reduced iron against carburization. Customers needed wrought iron since the decarburization processes of pig iron were not known yet. The composition of slag, mainly its FeO content, was essential for the degree of carburization of reduced metallic iron.

Granules of metallic iron have descended, together with slag, towards bottom of the furnace. Because of higher density granules of uncarburized iron descended faster – they moved with regard to slag.

The relative velocities of granules were determined by their size and the slag viscosity at 1200°C. Calculated velocities of descending granules of various sizes, calculated according to the Stokes law are presented in Table 1 (ρ_{iron} = 7800 kg/m^3, ρ_{slag} = 4000 kg/m^3).

Table 1: Influence of slag viscosity on the velocity of descending granules of metallic iron [mm/min]

	η [Ns/m^2]			
d [μm]	**0.01**	**0.05**	**0.1**	**0.2**
100	124	51	26	13
125	194	80	40	20
150	280	115	57	29
175	381	156	78	39
200	497	204	102	51

On the basis of samples from archeological investigations (microstructures shown at Figure 5 and Figure 6) it can be deducted that slag viscosity has influenced homogeneity of the bloom.

Phase boundary between the slag and the agglomerated iron is presented in Figure 5. This phase boundary is very uneven (irregular) since granules and iron conglomerates are united with the matrix in various spots, and thus more homogeneous lumps of iron are formed by the sintering in liquid slag. Single slag islands are visible in the iron. This slag was entrapped between the sintered granules or iron conglomerates, respectively. These in the iron entrapped slag remnants that were not squeezed out even with the forging process give evidence whether metallurgists in those times wanted to make harder or softer wrought iron. Slag contains many wustite dendrites in partially glassy matrix. There are visible single rounded iron conglomerates that did not sinter with the matrix yet.

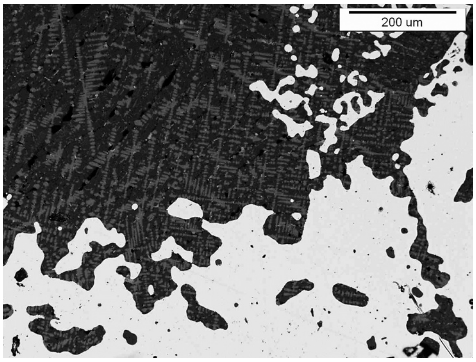

Figure 5: Phase boundary between the slag and the agglomerated iron

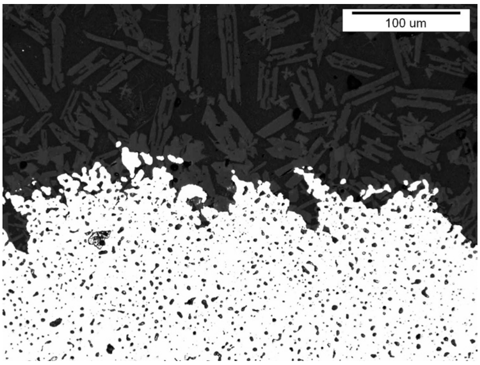

Figure 6: An uneven boundary between the metallic iron and the slag

Figure 6 also shows an uneven boundary between the metallic iron and the slag. In the sintered part of metallic iron there are numerous slag inclusions. The slag composition here also differs from that in the Figure 5 since it does not contain free wustite. The whole iron oxide is combined into fayalite that is in lamellar form in the glassy solidified matrix.

Slag had composition of fayalite or olivine (58 to 68 mass% FeO, 2 to 12 mass% CaO, 20 to 28 mass% SiO_2), respectively. The glassy solidified phase between fayalite crystals has composition: 45 to 55 mass% SiO_2, 12 to 20 mass % Al_2O_3, 2 to 5 mass% CaO, 12 to 24 mass% K_2O, and 8 to 15 mass% FeO. Slag contains FeO in form of dendrites or globules.

Slag compositions (chemical and phase) from production of wrought iron can be presented in $CaO–FeO–(Al_2O_3 – K_2O)–SiO_2$ system.

CONCLUSIONS

- The products of the bloomery process, representing direct process of making wrought iron, are liquid slag and solid wrought iron that gather in the furnace hearth.
- Important property of slag was that it prevented the carburization of reduced iron. It represented medium for transfer of granules of reduced iron towards furnace hearth where bloomery bloom was formed by sintering.
- The metallurgists in those times knew that additions of alkalis could control the viscosity and fluidity of slag therefore they used fluxes containing alkalis. Some alkalis came from the charcoal ash that introduced into slag calcium oxide as well as potassium oxide.
- Bloom is formed by the agglomeration with the sintering process in liquid slag. Sintering takes place by squeezing liquid phase from the spaces between granules of metallic iron.

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