PHENOMENOLOGICAL STUDY OF THE PLASMA REDUCTION OF IRON ORE IN HYDROGEN/ARGON-MIXTURES

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ABSTRACT

The aim of the work was the phenomenological investigation of the reduction process of iron ore and iron ore particles in a thermal argon/hydrogen-plasma as a function of hydrogen content and size. The main result is that a high temperature reduction mechanism occurs, which is characterized by forming iron nuclei equally distributed in the whole particle. Later on the iron agglomerates to an iron core surrounded by not fully reduced wüstite.

1. INTRODUCTION

The knowledge of the phenomenology of single particle reactions is one of the presumptions for the development of industrial plasma processes. Therefore we investigated the time dependence of morphological changes of iron ore particles which were treated in an argon/hydrogen-plasma environment.

2. EXPERIMENTAL

The reduction gas, argon with up to 6 vol% hydrogen, was heated in a 30 kW inductive plasma torch. The plasma properties in the quartz tube of 80 mm diameter were measured by probe and particle track methods. In the region of interest the upward flowing plasma was almost isenthalpic with a deviation of ± 5 % and changes in the concentration of the gas composition were negligible. The evaluation of the particle tracks yielded a flat velocity profile of 8 m/s. As all the essential features of the apparatus are similar to the setup we used for previous thermogravimetric investigations [1], no descriptions have to be given here.

In order to get an one-dimensional system we attached to a watercooled support a thin wire with a steel capsule, which was conically shaped downstream and, therefore, stabilized itself aerodynamically. The sample was embedded as a plate inside the front surface of the capsule exposed to direction of the plasma gas flow. The measurements of the surface temperature were performed pyrometically. To get information about the reaction progress, different samples were suspended to the plasma and quenched when the provided residence time was reached. To prevent reoxidation the sample was cooled in a non-oxidizing atmosphere. The progress of reduction in a hematite plate suspended stationary in a flowing plasma may differ appreciably from that of a particle moving freely through a plasma, as it will be the case in most of the proposed industrial plasma reactors.

Therefore, additional experiments with iron ore particles with a sieve fraction of 0.315 to 0.630 mm mesh size were made. After the particles were treated in the plasma with fairly constant properties of state, they were quenched in a non-oxidizing gas stream to prevent further reactions.

The reacted samples were embedded and prepared for microscopic analysis. To make the mineral phases visible, a gas-ion-contrast chamber was used. The samples were made of Itabira iron ore containing 66.9 % hematite and 9.1 % wüstite. The accompanying minerals amounted to 24 %.

3. RESULTS

In Fig. 1a a cross sectional cut through a partially reduced sample, surrounded above and on both sides by the steel capsule, is shown for a residence time of 10 s in an argon/hydrogen-plasma. It can be concluded that the reduction proceeds equidistantly from the surface into the hematite. The bright band that extends from the surface of the sample into its interior, consists of molten and dendritically solidified wüstite. The black spots in this bright sheet are holes that in the microscopic photograph appear as black as the embedding material below. In order to investigate the kinetics of the formation of the different phases, characteristic regions of the sample are shown with a greater magnification.

Fig. 1b shows typical wüstite dendrites surrounded by a silicate melt. The boundaries of the dendrites are partially reoxidized during the quenching processes.

In Fig. 1c can be seen, that the magnetite formation proceeds from the grain boundary. Fig. 1d shows hematite grains with a different morphological structure as a result of reoxidation. A typical low temperature reduction process due to a contact reaction between the steel capsule and the hematite shows Fig. 1e in the upper dark grey zones of the grains.

A characteristic cutout of a sample, which was suspended for about 20 s to the plasma, can be seen in Fig. 2a. The whole material has been reduced to wüstite. Only when this state of reduction is reached, first nuclei of iron are observed. We found them only on the boundaries of the wüstite dendrites. As the surface tension of iron is much higher then that of wüstite, the nuclei are connected by bridges and later on coagulate to drops. The start of these phenomena show Fig. 2b and 2c. The formation of spherical aggregates could not be observed under these experimental conditions, because the steel capsule is deformed normally after a residence time of about 25 s.

The reduction process taking place in the spherical particles falling through a plasma shows the series of crosscuts in Fig. 3a to 3f.

In Fig. 3a an original grain can be seen, while Fig. 3b to 3f show grains, treated all with a time of approximately 200 ms in a plasma, with rising hydrogen content up to 6 vol%. Fig. 3b shows a spheroidized hematite particle, reduced to wüstite in a plasma containing a low amount of hydrogen. The pore structure is not much different from that of the original grain. With rising hydrogen content in the plasma, the structure of the treated particles changes. Some larger pores can be seen and the typical dendritic structure becomes less significant.

In Fig. 3d we see iron nuclei formed under the same conditions as in the capsule experiments. It follows, that the formation of the nuclei does not proceeds from the particle surface, but occurs stochasticly distributed all over the whole particle. With further progress of reduction the iron agglomerates to larger drops as described above (Fig. 3e and 3f). Because of the great differences in the surface tension between iron and wüstite, no diffusion barrier of liquid iron to a wüstite core is formed, which is able to inhibit the reduction progress.

In process metallurgy the degree of metalization is an important feature. As a larger number of experiments was run, a statistical evaluation of the results was possible. With an opto-electronic device, attached to a computer, we calculated the iron content of the treated particles.

In Fig. 4 the volume percentage of iron formed is plotted over the hydrogen concentration. It can be seen, that with a hydrogen content of about 6 vol% the conversion to iron is about 20 vol%. The shape of the curve flattens out towards higher values of hydrogen indicating that under these experimental plasma conditions a reduction is possible with small amounts of hydrogen and that concentrations much higher than 6 vol% H_2 don't appreciably increase the yield.

A comparison of these results to values given in the literature [2,3,4,5] is difficult because of the different experimental conditions and materials. Nevertheless, it can be concluded that the mechanism of iron formation in particles treated by an argon/hydrogen-plasma has some features different from the reduction models for low temperature.

ACKNOWLEDGEMENT

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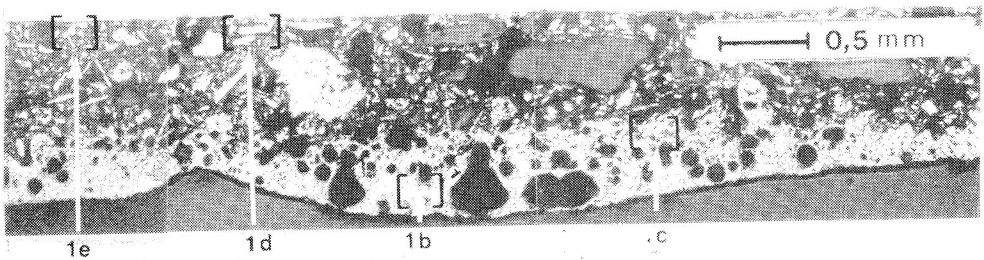

Fig. 1a: Micrograph of a partially reduced hematite sample: residence time-10 s, surface temperature in the stagnation point after 10 s -1450°C, local gas enthalpie-3.81 · 10^6 J/kg, local hydrogen concentration-3,5 vol%, local gas velocity-8 m/s.

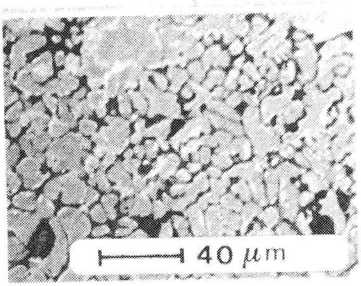

Fig. 1b: Solidified wüstite dendrites
white - magnetite
grey - wüstite
black - silicate melt

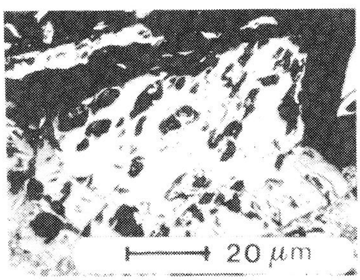

Fig. 1c: Partially reduced hematite grain
white - hematite
grey - magnetite
black - holes

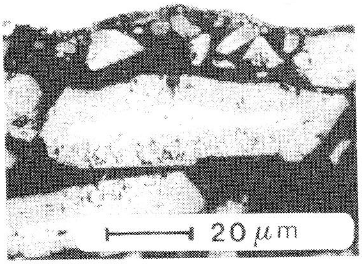

Fig. 1d: Reoxidized hematite grains
white - steel capsule
grey - hematite
black - holes

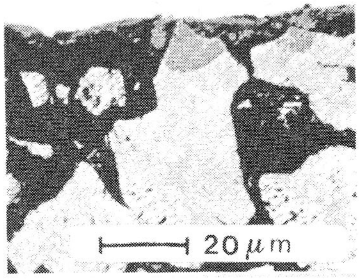

Fig. 1e: Hematite grains, reacted with the steel capsule
white - steel capsule
grey - hematite
dark grey - wüstite
black - holes

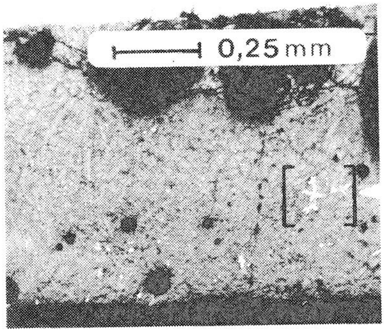

Fig. 2a: Cutout of the micrograph of a reduced hematite sample; residence time - 20 s, surface temperature in the stagnation point after 20 s - 1610°C, local gas enthalpie - 3.81 · 10^6 J/kg, local hydrogen concentration - 3,5 vol%, local gas velocity - 8 m/s

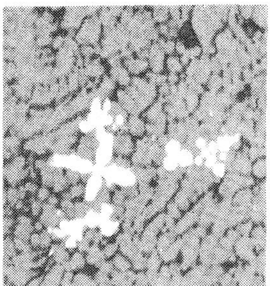

Fig. 2b: Iron nuclei
white - iron
grey - wüstite
black - holes, silicate melt

Fig. 2c: Magnification of Fig. 2b

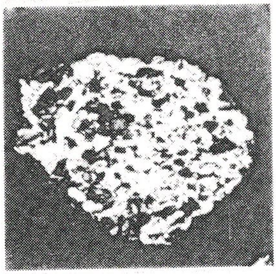

Fig. 3a: Original hematite grain
grey - hematite
black - holes, embedding material

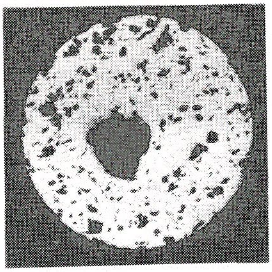

Fig. 3b: C_{H_2} = 0 vol%
white - iron
grey - wüstite
black - holes, embedding material

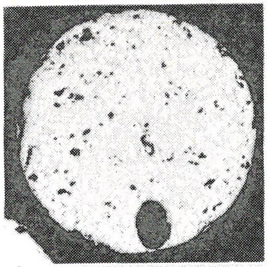

Fig. 3c: C_{H_2} = 0.9 vol%
white - iron
grey - wüstite
black - holes, embedding material

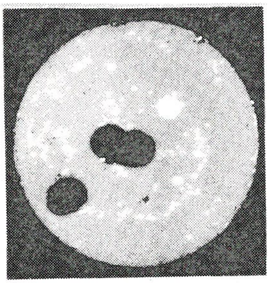

Fig. 3d: C_{H_2} = 1.8 vol%
white - iron
grey - wüstite
black - holes, embedding material

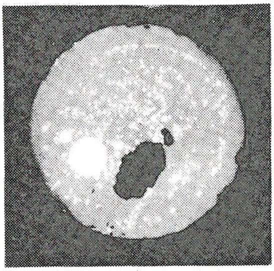

Fig. 3e: C_{H_2} = 3.5 vol%
white - iron
grey - wüstite
black - holes, embedding material

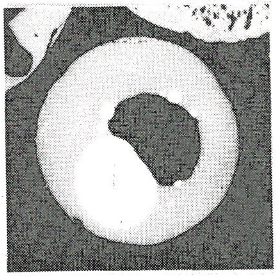

Fig. 3f: C_{H_2} = 5.0 vol%
white - iron
grey - wüstite
black - holes, embedding material

0,25 mm

Fig. 3 a-f:

Micrographs of an original nonreacted hematite grain and of particles, treated in an argon/hydrogen-plasma with different hydrogen contents C_{H_2}; sieve fraction of hematite particles with mesh size from 0.315 to 0.630 mm mean residence time ~ 200 ms

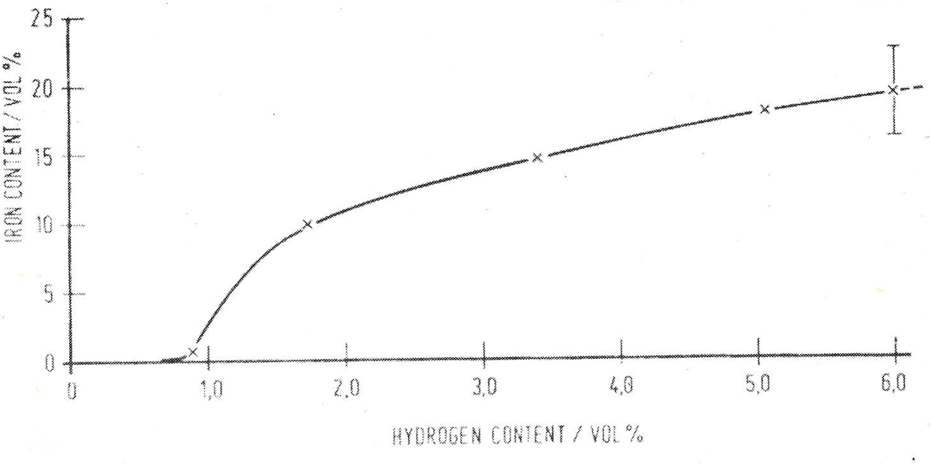

Fig. 4: Iron content of particles as a function of hydrogen concentration in the plasma; sieve fraction of hematite particles with mesh size from 0.315 to 0.630 mm, mean residence time ~ 200 ms