EFFECT OF COKE'S TEXTURE ON ELECTRICAL BEHAVIOR

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ABSTRACT

In submerged arc furnace (SAF) large volume of the feeding material consists of coke. Thus coke's electrical behavior plays an important role when considering the electrical behavior of SAF in ferrochrome production. In this work coke's electrical behavior is studied. The effect of coke's texture on the electrical behavior was studied using coke samples treated two different ways (simulated SAF atmosphere). Coke samples were treated using a) heat treatment at 950 °C and b) gasification by CO/CO_2 gas mixture. The effect of treatments on the texture and electrical behavior were studied using electrical measurements and compared to initial coke. It was found out that the heat treatment increase the graphitization degree and change electrical behavior of coke.

KEYWORDS: *Coke, electrical behavior, SAF, graphitization.*

1. INTRODUCTION

Submerged arc furnace (SAF) is a part in ferrochrome production process. The electrical behavior of the charge is important due to the effects on the productivity of furnace. The feeding material includes coke, chromite pellets and upgraded lumpy ore. This work concentrates on the effect of coke's texture on electrical behavior.

1.1 Coke making

The coal chosen for the coking process depends greatly on moisture, grain size, volatiles, ash concentration and different mineral concentrations. The coking process takes place in coking battery which consists of several coking ovens. The ovens are separated from each other by walls. The gas used for heating runs inside the walls. The coking process starts from the outer edge of the coke bed and proceeds to the center. The coking process ends when the center of the coal bed has been coked [3]. Width of the oven, coking temperature and coal's heat loss features affect the time that coking process takes [7].In the coking process the physical changes happen in the plastic zone (around 350 – 550°C) . First to happen is for the volatiles leave the coal [8]. First coal softens, melts, shrinks, extends and re-solidifies. After all the phases coal has turned into coke. Lastly the coke is cooled down from about 1000 °C to about 100 °C.

1.2. Electrical conductivity of coke

Graphite's structure is very organized one. This makes the electrical conductivity depend on the orientation of the atomic layers in graphite. Parallel to the layers electrical conductivity is similar to metal and perpendicular to the layers electrical conductivity is more like semiconductor [4]. Coke is not as structured as graphite. Thus electrical conductivity of coke is not as good as graphite [1]. Micro texture of coke has an influence on resistivity and reactivity. The lower the

resistivity the greater the local molecular orientation meaning more organized the micro texture. Furthermore reactivity increases when resistivity increases [12].

In the furnace the electrical conductivity of coke depends on the quality of coke. If coke comes from the edge of coking furnace it probably is more organized than if it comes from the center [10]. If coke selection is unsuccessful the electrical conductivity of charge can be too high in the upper part of SAF. Reorganization happens in coke bed when coke particles descend in SAF [9]. This may cause the decrease in electrical conductivity of charge. Conductivity starts to increase after the minimum [2]. This phenomenon has been seen in laboratory scale but it has not been confirmed in real SAF. Furthermore it is good to remember that coking temperature is about 1000 – 1300 °C. This means that in solid part of SAF coke particle will be exposed to temperatures that it has not been exposed before. Thus it can be expected that both coke particles structure and electrical conductivity increases.

2. EXPERIMENTS

The average composition of used coke is C-fix 87.2%, ash 11.9% and volatiles 0.8%. The grain size was over 19 mm. Coke samples were treated using a) heat treatment at 950 C and b) gasification by CO/CO_2 gas mixture. These treatments affect coke's texture by two different mechanisms which will be presented shortly. Coke samples were divided into three groups according to the way they are treated: 1) reference, no extra treatment for coke (raw), 2) coke treated with gasification (gas) and 3) coke treated with graphitization (graph). A list of measurements which were made for coke samples can be seen in table 1.

Table 1: A list of measurements made for samples.

Group	Sample n:o	Measurements
Raw	1, 2	Electrical measurements and XRD
	3, 4, 5, 6, 7, 8, 9, 10	Electrical measurements
Gas	1, 2	Electrical measurements and XRD
	3, 4, 5, 6, 7, 8, 9, 10, 11	Electrical measurements
Graph	1, 2	Electrical measurements and XRD
	3, 4, 5, 6, 7, 8, 9, 10, 11	Electrical measurements

2.1. Selective gasification

Gasification of coke was made in blast furnace simulator [5] in CO_2 atmosphere. First 108.65 g of coke was dried over 24 hours. Experiment started at inert nitrogen atmosphere and temperature raised from room temperature to 950 °C in 90 minutes. Then cokes were kept in CO_2 atmosphere at 950 °C for 240 minutes. Nitrogen atmosphere was again used in cooling period. Flow rate was 10 liters per minute. Electrical measurements were made for 11 coke particles and XRD measurements for 2.

Coke gasification degree was calculated to be 10.8% using equation 1[13]

$$x(t) = \frac{m_0 - m_t}{m_0 - m_0 \cdot A_{ad}} \cdot 100\% \quad (1)$$

where $x(t)$ is gasification degree, m_0 is coke mass in beginning, m_t coke mass at time t and A_{ad} coke's ash content. The change in mass during the coke gasification can be seen in figure 1. Total

mass decrease was 10.32 g which is about 9.5 %. The 0.5% change in mass in inert atmosphere at the beginning of the experiment is probably due to volatiles in coke.

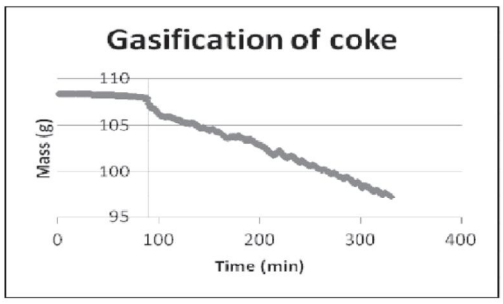

Figure 1: Mass change as a function of time in coke gasification experiment

2.2. Graphitization of coke

Heat treatment was made for coke amount of 93.24g. For the experiment coke was placed in graphite crucible which was placed inside corundum crucible (figure 2). Spinel and graphite lids were placed on top of the crucibles and the space between was filled with crushed graphite. Thus trying to insure that only temperature would affect the coke's texture. Then samples were kept in crucibles at 1600 °C air atmosphere for 24 hours. The rate of temperature increase and decrease was 10 °C/min. The mass of coke sample after the experiment was 83.90 g. XRD measurements were made for 2 coke particles and electrical measurements for 11.

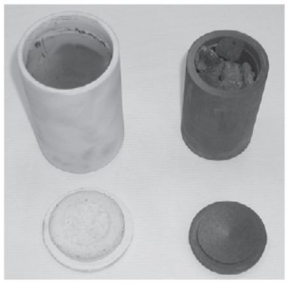

Figure 2: Crucible for coke in heat treatment experiment

3. RESULTS AND DISCUSSION

3.1. Coke graphitization degree

A sketch of structure for layers in graphite can be seen in figure 3. Graphitization degree is defined by the height of crystallites. Coke also has similar types of organized crystallites. By measuring the height of the crystallites (L_c) it is possible to give a numerical value for the graphitization degree [11].

Graphitization happens through four different stages. It is good to remember that transformation from one stage to another is quite quick. In the first stage the material consist of parallel centers which are situated arbitrarily. At the next stage around 800 – 1500 °C these parallel centers form pillar like structures. The height increases while the width stays the same. This is most typical level of organization for metallurgical cokes. Third stage around 1500 °C the layers start to merge and the height of the crystallites (L_c) increases. During the fourth stage graphitization is finished when the layers straightens [1].

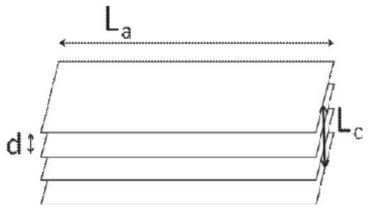

Figure 3: Structure of graphite crystallite (Modified from Sahajwalla et al[11])

3.2. Gasification of coke

Carbon solution loss reaction (gasification) of coke happens in oxidized atmosphere and high temperature. A simplified sketch of gasification can be seen in figure 4. Here the crystalline carbon and non-crystalline carbon gasify at different rates. Non-crystalline carbon gasifies faster compared to crystalline carbon. The graphitization of non-crystalline carbon happens at the same time. It is good to remember that graphitization rate increases when the temperature increases. Thus the reactivity of coke decreases when coking temperature and organization increases [6].

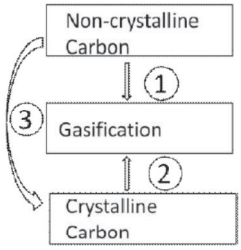

Figure 4: Gasification and crystallization of carbon (Modified from Kashiwaya and Ishii [6])

3.3. Electrical measurements

Electrical measurements were made with measurement device that be seen in figure 5. The coke particles were cut to hexahedron to achieve form of a cube. When the electrical measurements were made the coke particles were put between 20 mm x 20 mm copper plates for good contact. Measurements were made from all three directions and the resistance of the measurement device is subtracted thus achieving coke's average resistance and conductivity. Measurement results can be seen in table 2. It can be seen that if coke went through graphitization process then it has the highest electrical conductivity. The lowest conductivity is for coke that was gasified. Graphitization increases the average coke conductivity 97 % when compared to the raw coke. Also it is good to note the quite large variance between coke particles.

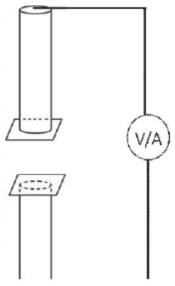

Figure 5: A rough sketch of measurement device (GW Instek LCR-817) for the electrical conductivity

Table 2: Electrical measurements for coke particles

	Average electrical conductivity [1/Ohm]	Max. deviation [1/Ohm]	Standard deviation [1/Ohm]
Raw coke	0.437	0.239	0.109
Graphitization	0.873	0.434	0.216
Gasification	0.382	0.184	0.100

XRD measurements were made for total of six coke particles. The particles were selected such that they resembled as close to a cube as possible. Examples of XRD spectra for raw, gasified and graphitized coke particles can be seen in figure 6.

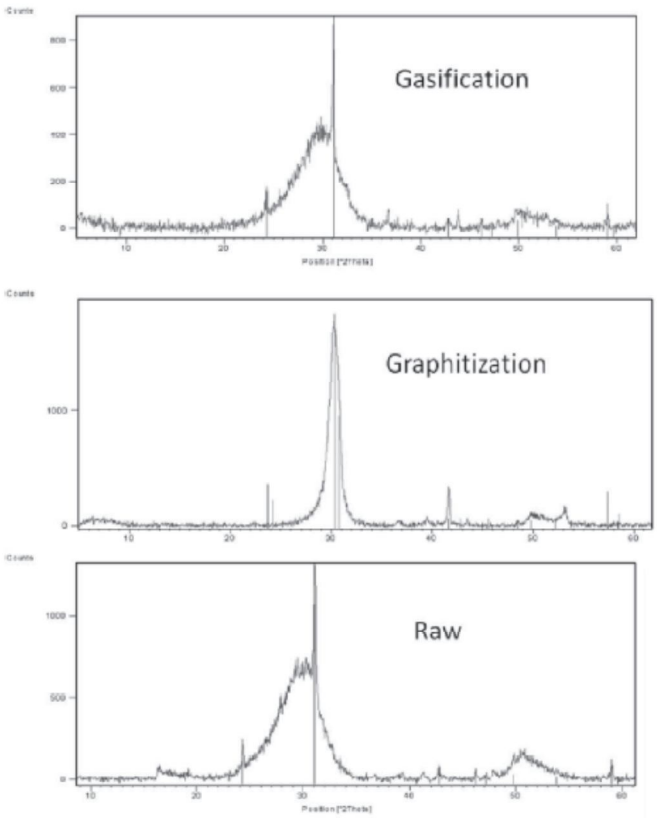

Figure 6: XRD spectra (gasification, graphitization, raw)

The graphite crystallites' height and width were defined using Scherrer equation, here equation 2 [6].

$$L_{c/a}(\text{Å}) = \frac{A\lambda}{B\cos\theta}, \tag{2}$$

where L_c is the height of the graphite crystallite, L_a is the width of the graphite crystallite, A is a constant given by reflection plane, λ is the x-ray wavelength [Å], B is the half-value width [rad] and θ is the reflection angle of peak. Note that L_{002}=0.9 and L_{10}=1.84. The height of the graphite crystallites as well as the width are compared to coke particle's electrical conductivity. Results can be seen in figures 7 and 8.

As can be seen from the figures the heat treatment increases the height of the graphite crystallites. Also graphitization of coke yields highest electrical conductivity of the compared samples. This is probably due to the greater height of graphite crystallites. Also heat treated coke samples had greater width of the graphite crystallites, but most likely this does not have as great impact on the electrical conductivity. Gasification does not increase the height of the graphite crystallites compared to the raw coke. Thus the electrical conductivity between those two groups does not have much difference. The width of graphite crystallites has less impact on electrical conductivity than the height of said crystallites.

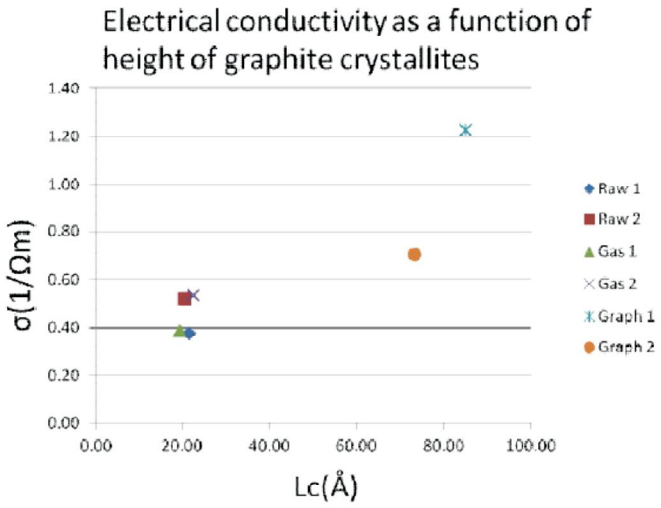

Figure 7: Height of graphite crystallites L_c as a function of electrical conductivity

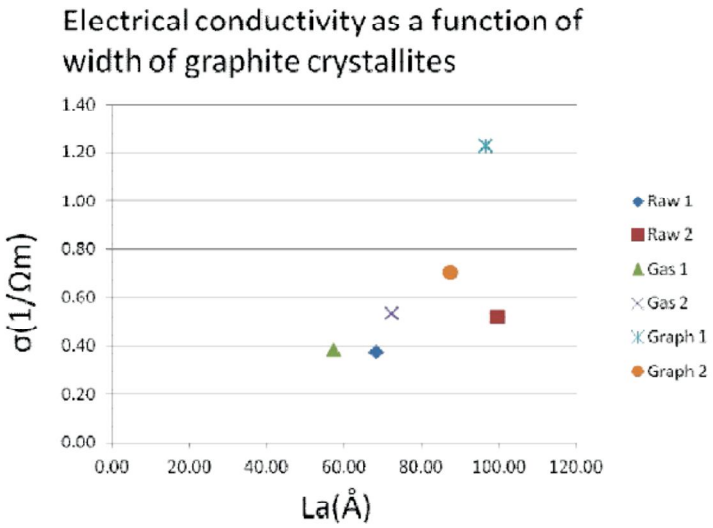

Figure 8: Width of graphite crystallites L_a as a function of electrical conductivity

It is known that pure graphite's structure is organized. During graphitization process the graphite crystallites' size increases. In this work coke was treated two different ways and then electrical conductivity was measured. We were able to change coke's structure towards more organized one by heat treatment. This could be seen from XRD measurements. Also it was found out that graphitization of coke (heat treatment) increases the electrical conductivity. On the other

had gasification of coke did not seem to have effects stated before. Gasification did not increase the size of graphite crystallites or the electrical conductivity.

4. ACKNOWLEDGEMENTS

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