

## Determination of crystallite size and influence of coke calcinations level on CO<sub>2</sub> reactivity and specific electrical resistance of coke

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**Abstract:** The average crystallite size ( $L_C$ ) is an important property of carbon materials for aluminum electrolysis.  $L_C$  is a useful factor to characterize the petroleum coke (PC) calcination level and in some cases to estimate the baking level of anodes. CO<sub>2</sub> reactivity of coke and specific electrical resistance (SER) are two important parameters in manufacturing of anode in aluminum industries. In addition the amount of sulfur and calcination temperature of coke is very effective. We demonstrate the effect of coke calcination with different sulfur level on CO<sub>2</sub> reactivity and specific electrical resistance. Many types of coke samples which were calcinated in different temperatures have been examined in this study. The  $L_C$  of coke samples has been estimated by the XRD then CO<sub>2</sub> reactivity and specific electrical resistance of coke were determined. Our data shows that when calcination of coke increases, CO<sub>2</sub> reactivity and specific electrical resistance of coke will decrease.

**Keywords:** crystallite size ( $L_C$ ), CO<sub>2</sub> reactivity of coke, specific electrical resistance, calcination level “,”

### Introduction

Carbon plays an important role in the industrial aluminum electrolysis. In recent years the quality of petroleum coke has been deteriorated. Economic consideration have therefore encourage a conversion to applications of cokes with higher sulfur content and coal tar pitch [1]. Calcined coke is produced when green coke is treated to higher temperatures (1200-1300°C). Coke is the most expensive raw material required for aluminum industries and has a strong influence on quality and quantity of aluminum.

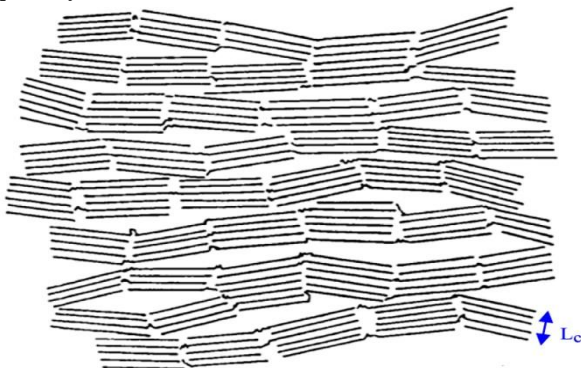


Fig. 1 Franklin model

There are several influence parameters on the coke. One of important parameters is crystallite size of coke ( $L_C$ ). One of the earliest models of the structure of disordered carbons, based on X-ray diffraction, was published by R.E. Franklin in 1950 [2] and 1951 [3].

The relative degree of anisotropy within carbon matrix has significant affects on the in- situ performance of the carbon filler within the anode. The parameter used to describe the quality of the coke structure from this

model is the crystallite size, described by the distances  $L_C$ . This is an estimation of the size of each individual crystallite (“graphite stack”) contributing to the diffraction of the X-rays.  $L_C$  is the distance along the c-axis, perpendicular to the graphitic planes (“crystallite height”);  $L_C$  is the one that is most relevant to carbon properties, and is also the easiest one to measure. It can be calculated by measuring the broadness of the main graphite peak in the XRD pattern. The  $L_C$  distance increases upon heat-treatment [4]. Some of the important parameters will affect on  $L_C$  such as sulfur level and calcined temperature. Figure 2 illustrate that  $L_C$  grow in nearly linear with calcination temperature and difference sulfur level.

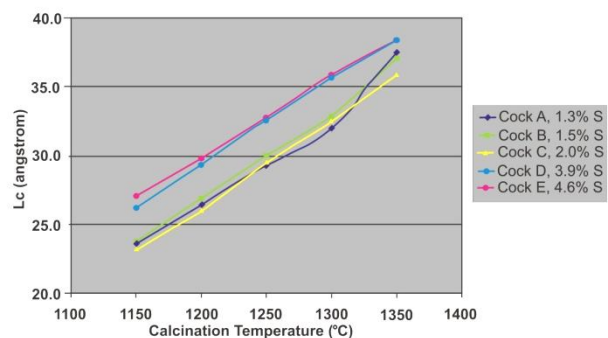


Fig. 2  $L_C$  development with calcination temperature for five cokes with different sulfur levels [5].

Two other important parameters for production of bake anode with high quality are specific electrical resistance and CO<sub>2</sub> reactivity of coke. The crystallite size has a great effect on the reactivity of coke. in this research it has

investigated about influence of different sulfur level in the coke on the  $L_C$  and also the effect of the  $L_C$  on the specific electrical resistance and  $CO_2$  reactivity of coke and finally we evaluate its effect on the quality of coke that increase the efficiency of aluminum production.

### Experimental

Materials: Boric acid and Hoechst wax C have made in Merck's Company

Equipments: X-ray diffraction (D4 Endeavor) and X-ray fluorescence (S4 pioneer) manufactured by Bruker Company of German. Coke Reflex and  $CO_2$  Reactivity apparatus manufactured by R&D Carbon Switzerland.

Entirely this part can divide into three steps that are such as:

- A) In determination of  $L_C$  by X-ray diffraction, the particle size of samples should be smaller than  $45\mu m$ . after the preparation of coke

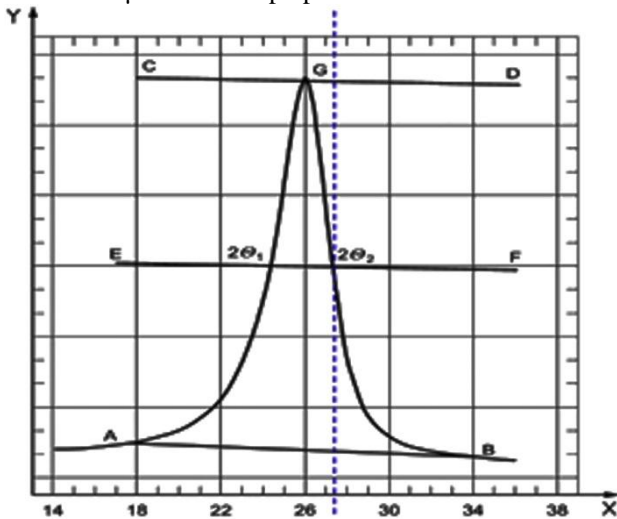


Fig. 3 Typical different scan of petroleum coke samples are calculated by XRD instrument with Scherrer method, [6]

$$\bar{L}_C = \frac{0.89\lambda}{\beta \cos \theta}$$

Where  $\beta$  is the peak integral breadth (IB) or full width at half maximum (FWHM) and  $\theta$  is the angle at the peak position. The figure 3 shows that a typical scan of petroleum coke.

- B) In the second step for measuring of  $CO_2$  Reactivity, a representative sample of calcined petroleum coke is taken from the whole in accordance with ISO Doc. 6375:

The particle size used in this test is 1-1.4 mm that and then the samples are dried at  $120 \pm 2^\circ C$  to constant weight. So  $5 \pm 0.001g$  of samples are weighted for the test measurement. Amount of the  $CO_2$  reactivity in % weight loss is calculated as follows [7]:

$$R_{CO_2} = \frac{\text{initial weight} - \text{final weight}}{\text{initial weight}} \times 100$$

- C) In the third step, SER is measured. The particle size and the time of drying is same as the second

step.  $15 \pm 0.001g$  of samples are weighted for the test measurement.

Many granular materials are coated with oil, for example to control dust formation during processing. If this is the case, the sample material must be rinsed with Dichloromethane before drying the oil according to the procedure outlined in ISO Doc.8723 [7].

### Results and Discussions

In this research 50 samples of calcined petroleum coke with different sulfur level have been analyzed in the same calcined temperature after that  $L_C$ ,  $CO_2$  reactivity and specific electrical resistance have been determined. This paper is arranged under two steps, at first the effect of sulfur level on the  $L_C$  and then the influence of the  $L_C$  on the  $CO_2$  reactivity and SER.

- 1- Effect of sulfur level on the  $L_C$  in constant calcined temperature

After determination of sulfur level in different calcination petroleum coke samples by XRF, the fluctuations of the  $L_C$  were considered with variety of sulfur level in the same temperature about  $1300^\circ C$  (figure 4).

The figure 4 illustrates that  $L_C$  growth in nearly linear in the same calcined coke's temperature, when the amount of sulfur increases. This increasing will continue until desulfurization temperature and after that the content of sulfur will decrease. Also it shows that more changes in  $L_C$  will occur when the amount of sulfur is more than 2.947%.

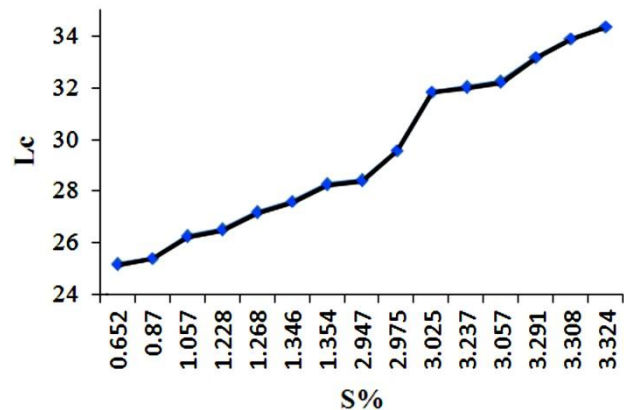
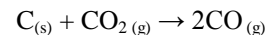


Fig.4 The effect of sulfur level on  $L_C$  in constant temperature

- 2- Influence of the  $L_C$  on  $CO_2$  reactivity and SER amount of the  $L_C$  have important effect on  $CO_2$  reactivity and SER. There are many reactions in bath and one of subsidiary reactions in  $900-960^\circ C$  is production of carbon monoxide.



After analyzing on more than 50 samples, the results were clarified whenever the amount of  $CO_2$  reactivity and SER decreased, the  $L_C$  increased.

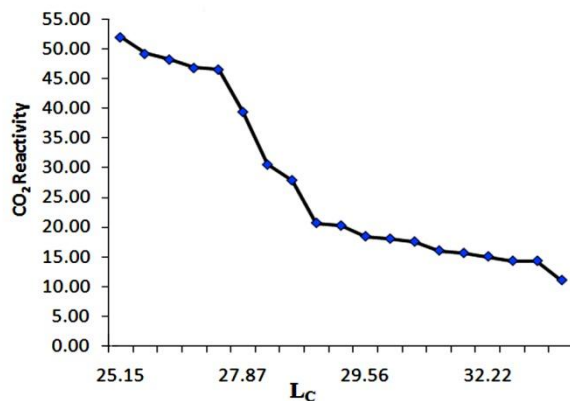


Fig.5 The dependence of the L<sub>C</sub> on CO<sub>2</sub> reactivity

According to definition of coke calcination CO<sub>2</sub> (g) will exhaust in the process. The rate of exhaust gas from PC is parallel with enhancing amount of L<sub>C</sub>. Base on above mention reaction (1) by increasing the L<sub>C</sub>, reactivity of coke with CO<sub>2</sub> (g) will be decrease and also figure 5 shows that when the L<sub>C</sub> is higher than 29.5A° the amount of CO<sub>2</sub> reactivity reduces well and will continue until L<sub>C</sub> 34.2A°. Figure 6 illustrates that SER will be decreasing because of increase the passing current. It points out that the best range of L<sub>C</sub> for SER is between 29.5A° to 34.1A°. in this range the rate of SER is between 445 to 503μΩm that is suit.

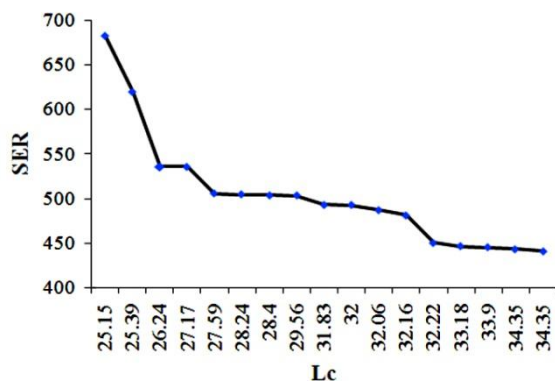


Fig.6 The dependence of the L<sub>C</sub> on ESR

## Conclusion

The calculation of L<sub>C</sub> values in different sulfur level show enhancing amount of sulfur of petroleum coke has direct effect on L<sub>C</sub>. The influence will continue up to desulfurization temperature. With increasing the L<sub>C</sub> two parameter CO<sub>2</sub> reactivity and SER will decrease. It can be predicted CO<sub>2</sub> reactivity and SER in the same condition by determination of L<sub>C</sub>. Based on the obtaining results, the best range of L<sub>C</sub> is between 29.5A° and 33.5A° and it is suggested that to be used instead of 28-30 A°.

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## Reference

- [1] K. Gjotheim, C. Krohn, M. Malinovsky, K. Mattiasovsky, J. Thonstad, Aluminum Electrolysis, 2nd Ed., Aluminum-Verlag, Düsseldorf, Germany, 1982, pp. 1-10.
- [2] R. E. Franklin, "The interpretation of diffuse X-ray diagrams of carbon", Acta Crystallographica 3 (1950) 107-121.
- [3] R. E. Franklin, "Crystallite growth in graphitizing and non-graphitizing carbons", Proceedings of the Royal Society of London, A209 (1951) 196-218.
- [4] S. Rorvik, L. P. Lossius and A. P. Ratvik, "Determination of coke calcination level and anode baking level- Application and reproducibility of L-sub-C based methods", The Minerals, Metals & Materials Society, (2011) 841.
- [5] L. Edwards, "Coke Property-Temperature Data, Rain CII Carbon LLC", Internal Report, (2010).
- [6] F. R. Feret, "Determination of the crystallinity of calcined and graphitic cokes by X-ray diffraction", Alcan International Ltd., Arvida Research and Development Center, Jonquiere, Québec, Canada 123 (1998), 595-600.
- [7] S. M. Hume, "Influence of Raw Material Properties on the Reactivity of Carbon Anodes", Ph.D. thesis, School of Engineering, University of Auckland, New Zealand. 1999, pp. 120-121.