Journal of Surface Engineered Materials and Advanced Technology, 2013, 3, 1-6
http://dx.doi.org/10.4236/jsemat.2013.33A001 Published Online September 2013 (http://www.scirp.org/journal/jsemat)

Determination of Coke, Pitch and Pores/Cracks in Green Anode by Image Analysis

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Received July 19th, 2013; revised August 22nd, 2013; accepted August 30th, 2013

ABSTRACT

Carbon anodes are an essential part of the primary aluminum production. They are made of coal tar pitch, calcined petroleum coke, recycled anodes and butts. As pitch acts as a binder for the anode, its proper distribution in a green anode has a great impact on the properties of the baked anode. Information on cracks in anodes is important for the quality of the baked anode. There is presently no reliable method available to analyze and quantify the amount of coke, pitch and pores/cracks in a green anode sample. In this article, an image analysis technique has been described, that can analyze as well as quantify the area percentage of pores/cracks and weight percentages of pitch and coke. The novelty of the method is its capacity to differentiate the different components of anode.

Keywords: Image Analysis; Carbon Anode; Coke; Pitch; Pore; Crack

1. Introduction

Carbon anodes for the production of primary aluminum are manufactured using coal tar pitch as binder with filler materials. The filler materials consist of calcined coke (fresh coke, recycled butts, and rejected anodes), pitch (coming from the rejected green anodes), and cokified pitch that has undergone baking and recycled in butts and rejected baked anodes). Thus, when the filler materials are mixed with fresh pitch to form the anode, the amount and the distribution of pitch change. It is a known fact that pitch quantity and distribution in an anode are two of the key factors defining anode properties such as density, electrical resistivity and CO_2/air reactivities [1,2]. There is no standardized technique available for the estimation of the pitch distribution in the anode samples.

Peterson *et al*. [3] showed that if the amount of pitch is above the optimum level, the width of the anode increases compared to the width of the mould. Thus measurement of the width of an anode can be correlated to the pitch content. Cracks are also studied by analyzing anode samples either by visual inspection or using optical microscopy or scanning electron microscopy. However, the indirect methods cannot be used to quantify the amount of pitch, coke, and pores/cracks.

Nowadays, researchers have presented an image analysis as a highly useful technique for the analysis; however, the challenge is that, in anodes, coke, pitch, and pores all appear black. Even with the scanning electron microscopy, it is hard to differentiate coke from pitch [4]. Researchers have proposed various methods of image analysis for coke (matrix and pore) and anode (coke matrix, pitch, and pore) by optical microscopy using polarized lights [4] or fluorescent materials [5].

Some commercial image analysis software is available for the analysis of different constituents in a material. The software provides different filters and image analysis techniques which need to be customized for identification of different constituents in an anode material. For example, the image analysis software developed at the National Institute of Health in the US [4] provides a filtering function (smooth, sharpen, find edges, etc.), rank filters (median filter to reduce noise, etc.), dither (to convert an image to a binary black and white image), spatial convolutions ("Mexican hat" filter which does both smoothing and edge detection in one operation), binary (convert gray scale image to binary), arithmetic and logical operations between two images, frequency domain display, subtract background, look-up table function (enhance contrast, equalize, etc.). Rorvik *et al.* [4] used this software to analyze coke, pitch and crack dis-

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tribution in a picture of a green anode sample taken using a polarized light and two filters. In their method, they relied on the Euclidian distance between the color of a point in the three-dimensional space of primary colors (red, green, and blue) with respect to the average value of pitch. In the software, the Euclidian distance map (EDM) is generated by replacing each foreground (black) pixel in the binary image with a gray value equal to that pixel's distance from the nearest background (white) pixel. However, the success of this method in identifying different constituents mainly depends on the proper selection of average values of pitch which can vary from sample to sample. Also, when a picture is binarized during analysis, a lot of information is ignored.

Adams *et al.* [6] proposed a semi-automatic method for the analysis of pitch in anodes. In the algorithm, they first converted the image to binary (black and white). Then they generated the dilated image filling the holes (black) of dimension less than 50 μm by the background color and analyzed pitch for only those particles which have an area greater than 100,000 μm^2. Thus, their method is applicable only to big particles. It may be noted that anodes often contain particles less than 75 μm in size. They used the optical microscope for the image analysis and, in the first stage, as they binarized the image, there was significant information loss.

Sadler [7] has developed a method of estimating cracks in baked anode samples using the optical microscope. The principle of the analysis was that if a light is applied at an angle of 30˚ with the surface of an anode sample, the cracks will be clearly visible. Thus, the cracks can be identified in a baked anode. However, coke, pore, and pitch cannot be identified separately by this image analysis technique.

Some researchers have applied image analysis technique to analyze pore distribution in coke samples. Rorvik *et al.* [5] proposed a method to analyze pores in coke particles by impregnating the particles by a fluorescent epoxy polymer. However, this method is hard to implement for anodes which contain pitch in addition to the pores/cracks.

Qiao *et al.* [8] developed an image analysis technique for analyzing pores in coke. They used Robert's edge detection algorithm followed by binarization and contrast stretching to identify the pores. They used an edge detection algorithm to identify the boundaries of pores and coke particles. As the pores appear more black compared to the coke surface, the contrast stretching technique was used to make the coke surfaces whiter. Then, a threshold value was chosen below which everything was poring. This method is hard to apply in the case of anodes as pitch also creates edges. It is also worth mentioning that pitch is black and its color is close to that of the pores, which makes this technique more difficult to implement in the case of anodes. Binarization can identify only two constituents. Therefore, the method cannot be directly applied for anodes.

This study focuses on the development of an image analysis technique that can be used to analyze pitch, coke, and pores/cracks distribution as well as to estimate the area percentage of pores/cracks and the weight percent of pitch and coke on the surface of a given green anode sample. This is based on the analysis of an image of the surface of an anode sample taken using the optical microscope and a light source from the side.

2. Materials and Methodology

2.1. Materials

A small cylindrical sample (diameter 50 mm and length 130 mm) from an industrial anode was used for the analysis.

2.2. Methodology

Green anodes are composed of coke, pitch, and pores/cracks. They all appear gray/black under white light. Therefore, it is very difficult to differentiate the three constituents. Moreover, the conventional methods rely on the analysis of the equivalent gray image of a colored image [4,6]. Any color can be expressed in terms of its primary constituents, namely red (R), green (G), and blue (B). The color scales can be expressed as integer values in the range of 0 to 255 for red, green, and blue separately. Thus 1.6 million (256 × 256 × 256) shades of color can be differentiated based on their R, G, B components. During the conversion of a color to its equivalent gray tone, the converted grayscale image may lose contrasts, sharpness, shadow, and structure of the color image [9]. That is why, in this work, the RGB image of the anode sample has not been converted to gray scale for the analysis of different components present in the anode sample.

2.3. Sample Preparation

A 1 cm × 1 cm anode sample was cut from the cylindrical sample and was placed in a small mould made of Teflon and was filled with epoxy resin mixed with an amine hardener (15:1). After 24 hours, the sample was taken out from the mould, and the surface containing the sample was polished using Struers Tegrapol-35 to have a smooth surface free from epoxy. The protocol proposed by Stuers [4], a commercial supplier of sample preparation equipment, was used for polishing the samples.

2.4. Instrumentation

The samples were examined using a standard inverted reflected light microscope (Nikon Eclipse ME 600 opti-

cal microscope), equipped with a motorized XY stage and focus controller. The stage movement and focus were controlled directly by commercial image analysis software (Clemex Vision Professional Edition software). A light source, incident at a specified angle, was used to illuminate the surface. Digital images were acquired using Power HAD Sony (3 CCD) camera and the images were saved using the Clemex Vision software. The zoom was set to 50× and the exposure time was maintained at 1/65 s.

2.5. Image Analysis

The captured image was analyzed using a software developed with Visual Basic 6.0.

2.5.1. Identification of Pores/Cracks

The pores/cracks were identified based on the work of Saddler [7]. If a light source is directed at the surface of an anode sample in an oblique angle, the light cannot enter significantly into the pores/cracks and creates a shaded region. The closer the light source is to the horizontal surface, the darker the pores/cracks appear compared to the coke and the pitch on the sample surface. The angle of incidence of the light on the green anode surface was chosen as 65˚ (see **Figure 1**) with the normal.

For each pixel in the image of the anode surface, the R, G, and B components were analyzed. Then, the threshold values were chosen for the R, G and B components in such a way that any pixel with R, G, and B components less than the corresponding threshold values was considered a pore/crack. The R, G, B values for a black pixel are 0, 0, 0 whereas, for a white one, they are 255, 255, 255. As the pores/cracks appear black, the threshold values should ideally be chosen close to zero. As some light can always enter into the pores/cracks due to the oblique incidence of the light source, the thresholds were chosen to have higher values. The threshold was selected after the analysis of different known anode samples.

2.5.2. Determination of the Position of Light

The angle of incidence of the light and its distance from the anode sample were determined based on the difference in the average brightness indices of pitch and pores/cracks, which is a measure of contrast. The color of coke is significantly different from those of pitch and pores/cracks; and the colors of pitch and pores/cracks are close to each other. Thus, the identification of the contrast between pitch and pores/cracks are more critical for the detection of pitch and pores/cracks in the anode sample. The luminescence index of a pixel is defined as (299R + 587G + 114B)/1000 where R, G, and B denote the red, green, and blue components of that pixel [10]. Web designers use this equation developed by the World Wide Web Consortium (W3) to calculate the color contrast [11]. In order to determine the optimum position of light source, the average values of brightness indices for pitch and pores/cracks were determined from an image of an anode sample where pores/cracks and pitch were clearly distinguishable. The difference between the average brightness indices of pitch and pores/cracks as a function of the distance as well as the angle of incidence (with respect to the normal) of the light as a function of the position of the anode sample under observation was determined. The position at which the contrast was maximum was used for the final analysis. These are discussed further below.

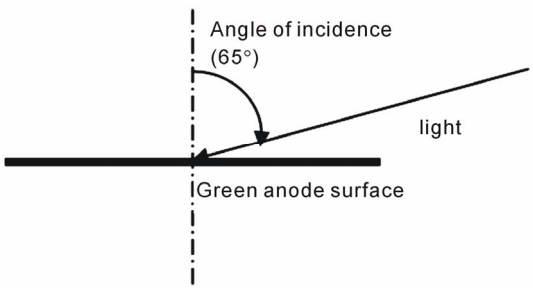

Figure 1. Angle of incidence of the light on a green anode surface.

The angles of incidence used for the study were between 60˚ and 70˚ because the light ray was obstructed by the lens of the microscope if a lower angle was used whereas the light touched the base of the sample holder if a higher angle was used. Regarding the distance, it was not possible to get closer than 20 mm because, at that distance, the shade of the light started to cover the lens of the microscope.

2.5.3. Identification of Coke and Pitch

After the identification of pores/cracks, the remaining pixels represent either coke (without pores) or pitch. By a series of experiments, the threshold values of R, G and B components were identified which can separate coke from pitch from the sample image. After identifying coke, all the remaining pixels will correspond to pitch. This threshold is dependent on the distance, the angle of incidence, color and the intensity of the light source.

For a given light source, these thresholds were calculated for known samples and later implemented for unknown samples to identify pores/cracks, coke, and pitch.

2.5.4. Calculation of Area Percentage of Pores

If the number of pixels satisfying the criteria for pores/cracks is N_{PC}, for coke (without pore) N_C, and for pitch N_P, then percentage of pores/cracks by area can be expressed as

$$\frac{N_{PC}}{N_{PC}+N_C+N_P}100 \quad (1)$$

2.5.5. Calculation of Weight Percentage of Coke and Pitch

The analysis of pixels gives results in area percentage of coke, pitch or pore. However, it is more convenient to express pitch and coke in terms of weight percentage because it is used in the anode preparation recipe and is better recognized by the industry. While calculating coke and pitch, the problem with pitch is that it can be on the coke surface or between two coke particles or within pore or crack. This causes the under-estimation of coke percentage since it hides the coke present just under this pitch layer. Therefore, the following correction was used to solve this problem. The pitch on the coke surface has been identified as those pixels satisfying characteristics of pitch but having at least one neighbor with properties of coke. Though this is an approximation, it helps determine the weight percentage of pitch and coke in the sample close to their real weight percent. If the number of this kind of pixels (yellow) is $N_{P/C}$, then it can be assumed that for ($N_C + N_{P/C}$) pixels of coke (without pores), there are N_P pixels of pitch. If ρ_C is the real density of coke and ρ_P is the density of pitch, then the weight percentage of pitch (W_P) can be expressed as:

$$W_P = \frac{N_P \rho_P}{(N_C + N_{P/C})\rho_C + N_P \rho_P} 100 \qquad (2)$$

Thus, the weight percentage of coke (W_P) will be 100-W_P.

Though the calculation of weight percent has some approximations, yet it gives a representative weight percent of pitch in a green anode sample.

2.5.6. Software for the Identification of Coke, Pitch, and Pores/Cracks

Identification of different components of coke was implemented by developing an application software using the Visual Basic 6.0. The point (x, y) method of the picturebox object of the visual basic has been used to analyze the RGB components of each pixel from the picture of the anode sample surfaces. After analyzing different components based on the thresholds, pixels corresponding to pores/cracks, coke and pitch were marked separately.

3. Results and Discussions

Figure 2 shows the picture of the anode which was used to study the effect of position of the light source.

Figures 3 and **4** show the effects of the distance and the angle of incidence of light on the contrast, the difference in the average brightness indices of pitch and pores/cracks, respectively. The distance was studied for a constant angle of incidence of 70˚. As the highest contrast was observed for a distance of 20 mm of the light from the position of the sample under observation, this distance was maintained later onto measure the angle of incidence.

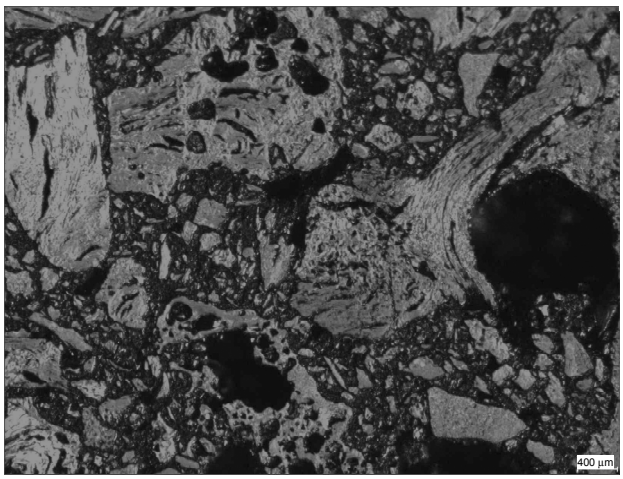

Figure 2. Sample image, taken by optical microscope, used to study the position of light.

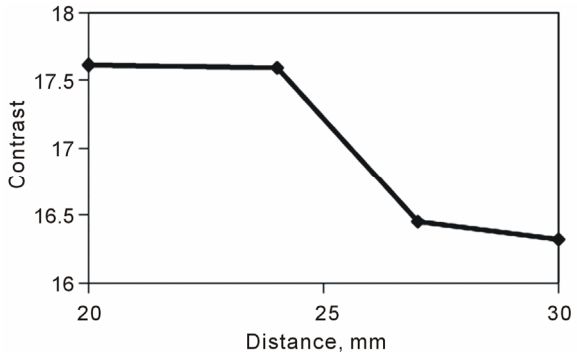

Figure 3. Effect of the distance of light on contrast between pitch and pores/cracks.

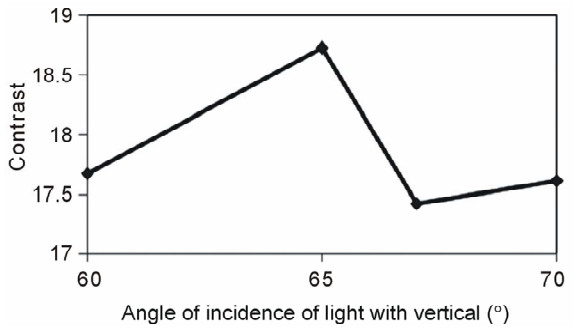

Figure 4. Effect of the angle of incidence of light on contrast between pitch and pores/cracks.

It can be observed from **Figures 3** and **4** that the maximum contrast is achievable with an angle of incidence of 65˚ and at a distance of 20 mm. Thus, this position was maintained for the light source for further analyses of other images. Also, **Table 1** shows the thresholds used for the image analysis.

Table 1. The thresholds for the image analysis.

Threshold for pore			Threshold for coke		
R less than	G less than	B less than	R greater than	G greater than	B less than
15	40	90	20	10	73

Figure 5(a) shows the image of a green anode sample taken by the optical microscope. **Figures 5(b)-(d)** show the distributions of coke, pitch and pores/cracks separately for the image given in **Figure 5(a)**. From the image analysis, the pore area was determined as 14.25%. The weight percentages of pitch and coke were found as 13.83 and 86.17, respectively. Since the image analyses give the area percentage which is assumed to be same as the volume percentage, the weight percentages were calculated assuming real densities of 1.32 g/ml for pitch and 2.06 g/ml for coke.

In order to compare with the percentages obtained from the image analysis, the pores/cracks volume percentage was calculated for the sample. Coke at 86.23 wt% with a real density of 2.06 g/cc was mixed with pitch at 13.77 wt% with a density of 1.32 g/cc to prepare the anode sample.

Thus, the volume (without pores/cracks) of 100 g of the anode sample

$$= \frac{86.23}{2.06} + \frac{13.77}{1.32}$$

= 59.29 ml.

And the real density of the green anode sample

$$= \frac{100}{59.29}$$

= 1.91 g/ml.

The bulk density of the sample was measured as 1.64 g/ml.

Hence, the volume percentage of pores/cracks

$$= \left(1 - \frac{1.64}{1.91}\right) \times 100$$

= 14.23.

The measured value with the current image analysis software was 14.25, which compares favorably with the experimental value of 14.23. The pitch weight percentage measured with the current image analysis software was 13.83, which was very close to the experimental value 13.77. This shows that the results of the image analysis method proposed in this article are in good agreement with the experimental values.

The method worked successfully for the analysis of other images taken with the optical microscope under similar conditions. The novelty of the method is the application of light source to distinguish pitch, coke, and pores/cracks on the surface of an anode sample. **Table 2** gives the comparison of this method with other published works.

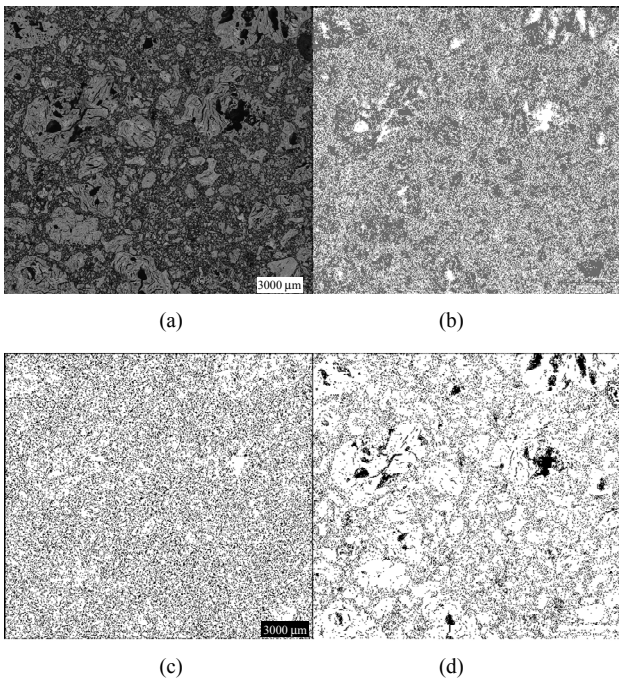

Figure 5. (a) Image of an anode sample taken with the optical microscope; Analysis of the sample shown in Figure 5(a): (b) coke distribution; (c) pitch distribution; (d) pores/cracks distribution.

4. Conclusion

A novel method of analyzing pitch, coke, and pores/cracks in a green anode sample has been developed and described. The uniqueness of the method is the use of a light source to identify the three constituents in a green anode sample. Though there are certain approximations, effort has been made to calculate the weight percentage of pitch and coke in the green anode sample. The results are in good agreement with the actual amount of pitch weight percentage in the anode samples. The percentage area covered by pores/cracks has also been calculated. The threshold values depend on the color and intensity of light, the position of light, and the image capturing device. Thus, for a specific set of light inclined at a fixed angle and for a specific camera, the thresholds will become constant. Therefore, the system can be used to analyze other green anode samples with the same settings of the parameters, making the system sample-independent.

5. Acknowledgements

The technical and financial support of Aluminerie Alouette Inc. as well as the financial support of the National

Table 2. Comparison of current method with the published ones.

Method	Identifies	Application	Reference
Identification of grain boundary, contrast stretching, and binarization	Pores in coke samples	Suitable for two constituents only, thus not suitable for identification of coke, pitch, and pores/cracks in anodes	[8]
Used fluorescent epoxy	Pores in coke samples	Suitable for two constituents only, thus not suitable for identification of coke, pitch, and pores/cracks in anodes	[5]
Binarization	Pitch in anode	Suitable for large particles only using an optical microscope	[6]
Distance of color from average color value for pitch	Pitch, pore, and crack	Success depends on the choice of average color value of pitch which can vary from sample to sample	[4]
Light creates shadows at places of cracks	Cracks	Not capable of identifying pitch and coke, no quantitative estimation	[7]
Application of light to identify pores and cracks, threshold value to identify coke and pitch	Pitch, coke, pore and crack	Capable of analyzing pore area percentage and coke and pitch weight percentage.	Present work

Science and Engineering Research Council of Canada (NSERC), Développement économique Sept-Îles, the University of Québec at Chicoutimi (UQAC), and the Foundation of the University of Québec at Chicoutimi (FUQAC) are greatly appreciated. The authors would also like to thank Dr. Samir Sahli for his valuable suggestions on the improvement of the efficiency of the analysis.

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