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A METHOD FOR THE RAPID CHARACTERIZATION OF PETROLEUM COKE MICROSTRUCTURE USING POLARIZED LIGHT MICROSCOPY

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Abstract

Petroleum coke is used for the fabrication of anodes for aluminum reduction cells. There are ever-increasing economic and supply availability pressures for alternative and multiple sources and qualities for fabricating anodes, and therefore for cost effective characterization to make timely adjustments of the anode mixes. One characteristic historically acknowledged as having a significant detrimental influence on anode thermo-mechanical properties is the so-called isotropic structure. Traditionally such characterizations using optical microscopy are exhaustive and therefore cause a throughput concern. A method was developed and successfully applied to green and calcined coke reducing the interpretation time of a sample down to about twenty minutes. The sample preparation and interpretation methodology is described and examples presented, including a case study of how the method was used to guide raw material blend decisions across Rio Tinto Alcan's North American sites.

Introduction

The aluminum industry faces a shortage of anode-grade coke. However, just one quarter of the green coke available is presently considered anode-grade [1]. Some cokes of the remaining three quarters are not used since their texture is believed to be unsuitable for anodes. An important concern with isotropic and near-isotropic (granular) cokes is their high coefficient of thermal expansion (CTE) which makes anodes more susceptible towards thermal shock cracking [2]. However, in the present short coke market, calciners have started to use highly isotropic cokes in their blends [3]. Furthermore, successful tests with shot coke, also very isotropic, in medium-amperage pots were reported [4]. Apparently, certain quantities of isotropic cokes can be tolerated in anodes. This may open the opportunity to enlarge the coke supply base.

Another development is that the coke quality, including shipments from long time suppliers, fluctuates much more than in previous years. For example, between 0 and 60% isotropic cokes are now observed in samples from a Rio Tinto Alcan green coke +30 years supplier. In order to improve their economics, many refineries are buying an increasing share of their feed on the spot market. The varying feed quality translates to unstable coke quality. It is therefore necessary that the coke quality is closely followed by the coke user.

The above discussion illustrates that a reliable characterization method for the coke texture is required. In an industrial setting, laboratory throughput is a major concern. Ideally, the interpretation time (*i.e.* sample observation and interpretation, excluding sample preparation) should be as fast as possible. A target of less than half an hour is preferred.

Coke Texture Classification

For metallurgical coke, a texture classification has been accepted by ASTM [5]. For petroleum cokes, however, several systems are used, among which the optical texture index (OTI, Table 1 and Eq. 1) has been used [6-8]. The OTI was found to correlate with the coke CTE [7]. However, quantification of the ten texture types required for the OTI corresponds to an interpretation time of several hours, which is not practical in Rio Tinto Alcan's context.

Table 1
Coke textures used to calculate the optical texture index (OTI) of petroleum coke [6]

	Texture	Size	OTI of texture
1	Isotropic	No optical activity	0
2	Fine-grained mosaics	<1.5 µm	1
3	Medium-grained mosaics	1.5-5 µm	3
4	Coarse-grained mosaics	5-10 µm	7
5	Medium-flow anisotropy	<30 µm length, <5 µm width	7
6	Supra mosaics	Aligned mosaics	10
7	Small domains	10-60 µm	20
8	Coarse-flow anisotropy	30-60 µm length, 5-10 µm width	20
9	Domains	>60 µm	30
10	Flow-domain anisotropy	>60 µm length, >10 µm width	30

$$OTI = \sum_i (f_i \cdot OTI_i) \qquad \text{Eq. (1)}$$

Where f_i is the fraction of a texture and OTI_i its texture index.

An alternative could be an automated system [9,10]. However, based upon experience with image analysis systems it was felt that set-up of a robust automated method would require considerable effort and would not necessarily yield a significant time advantage. Furthermore, some cokes recently evaluated by Rio Tinto Alcan had "non-standard" textures, such as intermediates of sponge and shot coke textures, which might not be recognized by a fully automated system.

While OTI has been used, in general a wide range of methodologies have been used [11]. There is neither a recognized standard nomenclature nor a quantification technique applicable to the interpretation of petroleum coke texture; the methodology applied appears to be at the discretion of the laboratory as a function of analytical needs. In that respect the needs of the Rio Tinto Alcan organization are as follows:

1. To screen samples of in-coming lots and of new candidate sources for the presence of undesirable

texture, and microstructure, *e.g.* highly porous such as in Figure 1.

2. To discern trends that could significantly affect anode performance.
3. To provide such information in a timely fashion for decision making by management to take advantage of spot market conditions.
4. To minimize the burden on available laboratory resources.

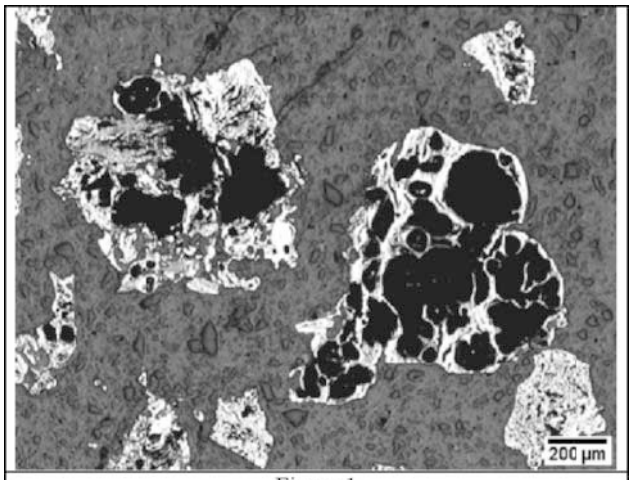

Figure 1
Micrograph (non-polarized light) showing an example of a highly porous calcined coke grain, termed "pop-corn" within Rio Tinto Alcan.

Rio Tinto Texture Classification System

Considering the observation time in the order of six hours required to determine the OTI this technique was ruled out for routine analysis. Thus, instead of the ten texture types listed in Table 1, just three textures types are quantified in routine analysis by Rio Tinto Alcan. This system can be considered as a simplified OTI system since its texture types comprise several OTI texture types (Table 2). By the simplification some information is lost, especially with respect to anisotropic textures. Nevertheless, such a simplification still allows to sufficiently predict the anode CTE [12].

Finally, note that the nomenclature for the textures used by Rio Tinto Alcan differs from that used by other groups [12], due to the laboratory's characterization of other material types. For instance an amorphous material, e.g. Figure 2, has no optical activity, and is called isotropic instead of fine granular coke.

Table 2
Coke textures used in simplified Rio Tinto Alcan classification system

Texture	Corresponding textures in OTI system	Size	Figure
Amorphous	1	No optical activity	2
Isotropic	2-3	Length ~ width, <5 microns	3
Anisotropic	4-10	Length > width, >5 microns	4

Examples of different textures of the simplified Rio Tinto Alcan classification system. Micrographs recorded with polarized light

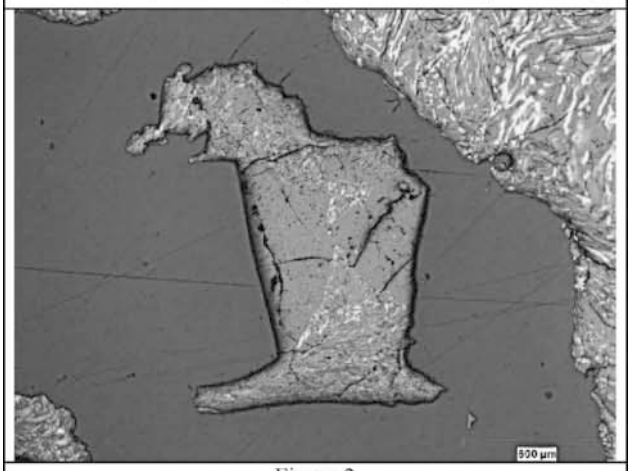

Figure 2
A coke grain containing regions that are amorphous, *i.e.* no texture. Micrograph taken at 50 X.

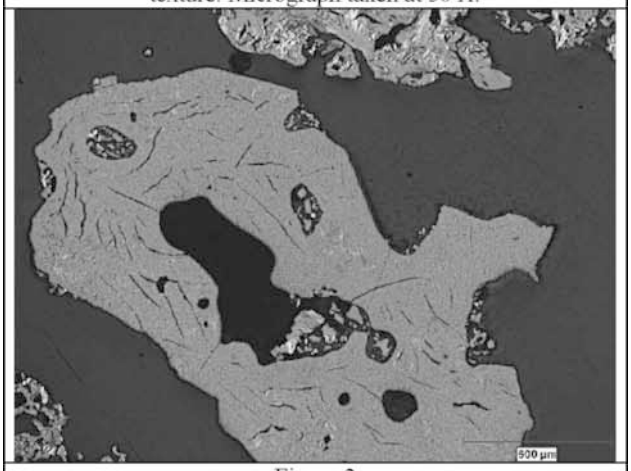

Figure 3
A coke grain with an assigned isotropic texture. Micrograph taken at 50 X.

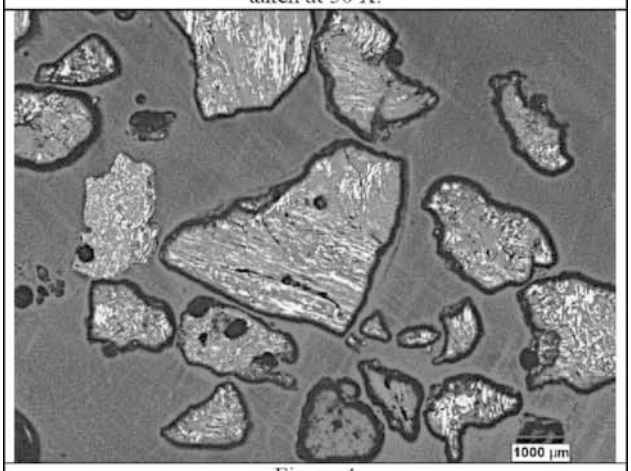

Figure 4
Fine particles of calcined coke illustrating pronounced anisotropic textures. Micrograph taken at 25 X.

It took several iterations before arriving at the characterization method presently used. Key considerations contributing to an analysis time of less than 30 minutes per sample are as follows:

- Establishing a visual limit for unacceptable texture
- Magnification selection
- An optimum particle size of the coke grains
- A visual assessment method

These items are briefly discussed in the next sections.

Texture Type Limit

As previously mentioned, it is well appreciated and widely accepted that the stronger the anisotropy of coke the better it is for anode performance.

When viewed using a polarized light microscope, isotropic materials are considered to be optically inactive, *i.e.* no discernible features are observable. However, to discern if a material is optically inactive, high magnifications are typically advised which, due to inherent requirements that will be discussed in the next section, can slow down the evaluation process. Our desire was therefore to use lower magnifications. In so doing resolution is reduced and anisotropic textures, such as fine grained mosaics are not readily discernible. Even so, it can be argued that such fine-grained and even medium-grained mosaics, that are near isotropic, would not necessarily be significantly better for anode performance. In fact, all OTI texture types that contribute to the isotropic texture in the Rio Tinto Alcan system have low OTI values (between 1 and 3, Table 1), corresponding to high CTE values.

As a result, in consideration that this is a screening tool, and to avoid high magnification verifications by the microscopist, the term "isotropic" applied in Rio Tinto Alcan results includes textures that are just apparent at the magnification used, e.g. up to Type 3 in Table 1. An example of this condition is given in Figure 5.

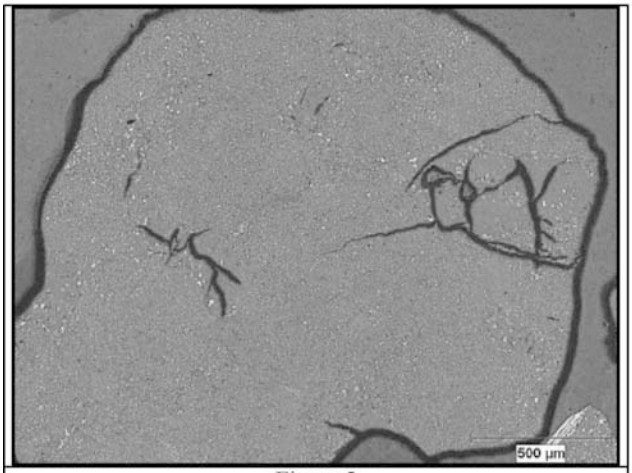

Figure 5
Green coke grain with a predominant texture that is apparent at the scanning magnification. Micrograph taken at 50 X.

Magnification Selection

To discern if a coke grain is optically inactive, *i.e.* no features resolvable by optical microscope with polarized light, magnifications up to about 1000 X and higher if possible, with oil immersion lenses, are advised to see if there are features as small as about 0.5 microns. The Rio Tinto Alcan Arvida R&D Centre is not equipped with oil immersion lens capability. Even if it was, the use of such lenses was considered as a throughput hindrance considering the number of fields of view used for obtaining a reasonable portrait of texture in a sample, placing oil droplets, and delicately applying fine focus due to the short working distance between lens and specimen surface. Even with air lenses, high magnifications require more care when fine focusing. More care in focusing equals more time.

As a further consideration for choosing a low magnification, the interest is to have a sense of what the 'forest' looks like and not to seek detail of the 'trees'. Coke grains can often have a mixture of textures; an example is given in Figure 6. As a result, by and large, the evaluations are done at 25 or 50 X with, on occasion, if needed, checks at higher magnification typically not exceeding 200 X. The working distance with those magnifications is such that the entire sample can be evaluated with little to no refocusing. However, to facilitate this process it is beneficial if the coke grains are within a specific window of dimension.

Coke Grain Size

To be able to work with low magnification lenses, coke grain size becomes a consideration. If the grains are too small, more time is needed to look at each grain, assess, and note texture. This can be appreciated in Figure 4. If the grains are too big, the entire grain may not be within the field of view, and/ or that more time is needed to appreciate the various texture types within the grain. Based on these considerations, Rio Tinto Alcan performs routine analysis on grains between 4.75 and 1.7 mm (- 4 to + 10 mesh). It was confirmed that the texture of these particles is in general representative for all particle sizes.

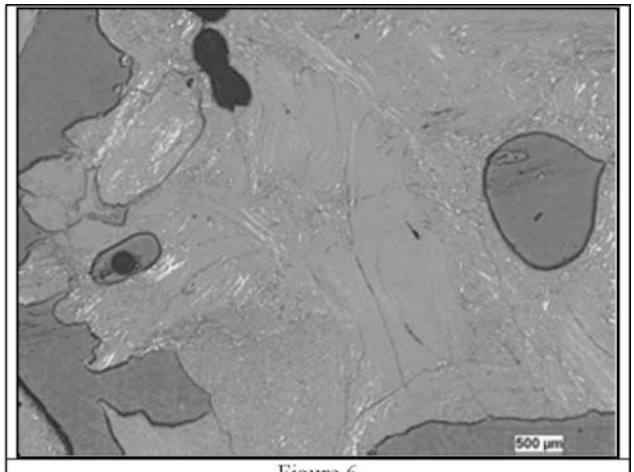

Figure 6
Green coke grain with various texture types, of which about half is assigned as isotropic. Micrograph taken at a 50 X.

Visual Assessment

Initially an assessment technique similar to that for OTI (Table 1)

was done. Each polished mount took in excess of half a day to characterize. Another method tried used a 10 x 10 grid graticule in a microscope eyepiece to obtain area occupation values using various scanning schemes. For instance at 50 X magnification the entire grid would overlay an area viewed of 1 mm x 1 mm, or each division would cover an area 100 microns by 100 microns. The area occupied by a given texture type is determined by its area of occupation within the grid for each of the 100 respective fields examined. This process was again time consuming and, in the end, it was demonstrated that the results were not necessarily significantly different from simply looking at the microstructure and judging by eye (Table 3). The human eye-mind connection can be a very powerful analytical tool, so that once the eye knows what to look for, the mind of a microscopist can estimate within a few percent fairly reliably, at least to the extent needed for screening. Usually it takes just a few seconds per grain to register the mind's eye interpretation.

Table 3
Comparison of results using a 10 x 10 grid graticule and visual estimation

Sample	Measured concentration of isotropic textures [%] [a]	
	10 X 10 grid	Visual estimate
1	53	50
2	53	50
3	7	10 to 15

[a] No amorphous coke found, remainder is anisotropic coke

The estimation process has two rules of thumb to simplify the evaluation:

- If a given texture comprises ≥ 70% of a grain's surface, that texture is assigned to the entire grain. For instance if a grain has at least 70% of an isotropic appearance, it is counted as an isotropic grain.
- If a given grain does not have predominantly one texture type, *i.e.* both constitute < 70% of the surface area, then half is assigned as isotropic and half is assigned anisotropic. See Figure 6 for an example.

The full and half grain counts are totaled and percentages provided relative to the total number of grains assessed.

If the grain size is such that fewer than about 100 grains are present in a mount, all are assessed. If there are more than 100 grains, 100 are assessed and, if warranted, more. In this way a reasonably good portrait of the coke sample is obtained within about 20 minutes of evaluation. Both green and calcined cokes are assessed routinely – over 200 samples in 2011 by a single microscopist in the Rio Tinto Alcan Arvida laboratory.

Since the introduction of this method, additional refinements have been incorporated in the reported results with respect to the semi-quantification of the stronger anisotropic textures, without significant penalty to the evaluation time. The value of this information is under assessment and may be the subject of a future publication.

An additional advantage of such an overview technique involving numerous grains is the greater probability of encountering foreign material, *e.g.* Figure 7, and unusual textures, *e.g.* Figure 8.

The particle presented in Figure 7 was identified by subsequent energy-dispersive X-ray spectroscopy (EDX) analysis to be iron oxide. Probably, it is the result of contamination during coke storage or transport.

The particle shown in Figure 8 is believed to be an intermediate between sponge and shot coke. The isotropic spherical features, typical for shot coke [13], are easily recognizable in the micrograph. However, by visual inspection of this coke, no characteristic shot coke beads were found. This is important since some Rio Tinto Alcan suppliers occasionally produce batches containing shot coke. Shipments from these suppliers are routinely analyzed for shot coke by visual inspection. However, as shown here, the inspection might fail to identify "near shot coke" structures. As opposed to fully automated microscopic analysis, a microscopist can catch and flag these anomalies.

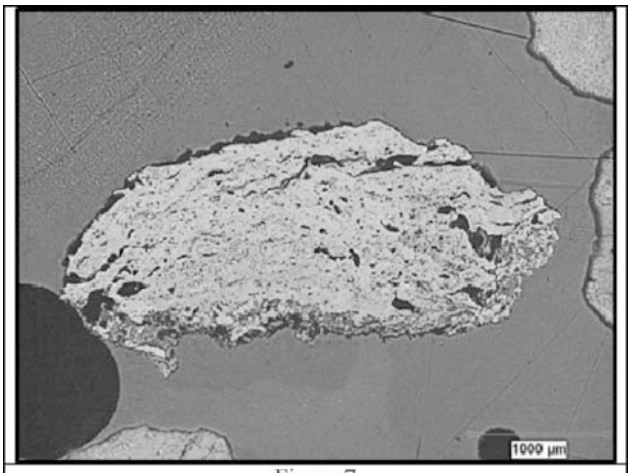

Figure 7
Example of foreign material encountered during an evaluation, determined to be iron oxide in this case. Image taken at 25 X.

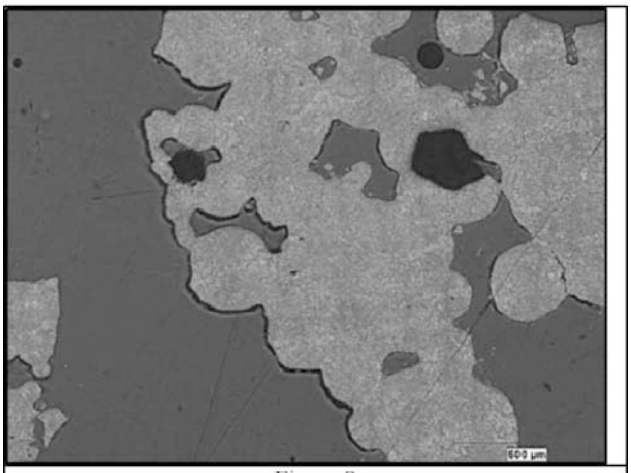

Figure 8
Example of an unusual texture, possibly attributable to shot coke. Micrograph taken at 50 X.

Sample Preparation

As outlined in the previous sections, considerable effort was spent to reduce the sample observation time. The sample preparation procedure, however, did not need to be changed. Shortening the

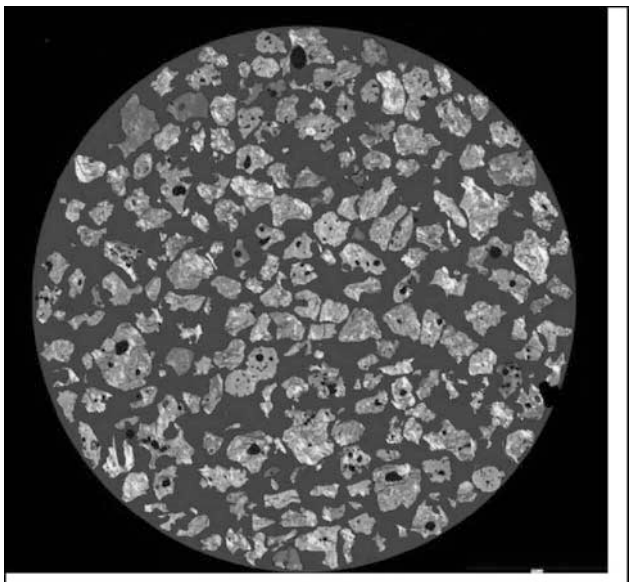

Figure 9
A mosaic of 80 images showing the entire surface of a polished mount of calcined coke grains.

preparation time would have resulted in loss of micrograph quality, which is critical for sample evaluation.

The coke particles are mounted in epoxy resin to cure overnight. The 38 mm diameter mounts are prepared using an automated polishing system with a multiple sample holder. They are first ground using a progressively finer sequence of SiC abrasives, then an intermediate polish with diamond abrasives, and a final polish with an alumina suspension. The total polishing time is in the order of 15 to 20 minutes. Figure 9 has a mosaic of images showing the surface appearance of an entire polished mount.

Industrial Application

The use of this evaluation technique has allowed Rio Tinto Alcan procurement and technical management to make decisions with respect to spot market opportunities, and to help follow the consequences of those decisions with respect to anode quality.

The simplified method described here was used to quantify the concentration of amorphous and isotropic coke in all of its green and calcined coke sources. Most of them were found to contain only few amorphous and isotropic textures. However, some coke sources contained significant concentrations of these textures. Furthermore, important fluctuations were observed [3]. Shipments from certain suppliers are therefore now closely followed by microscopy analysis.

It is known for laboratory anode tests and plant experience what concentrations of amorphous and isotropic coke are still acceptable. If necessary, coke allocation is modified ensuring that the concentration of these textures stays below critical values.

Concluding Remarks

As a response to the market pressures for using alternative and multiple sources and qualities of green and calcined coke, Rio Tinto Alcan developed and is successfully applying a non-traditional optical microscopy method for their characterization. The microscope time for the evaluation takes about 20 minutes. The method provides sufficient information for screening and seeing trends with respect to the presence of undesirable amorphous and isotropic textures, while at the same time lessening the human resources burden that would be experienced in using the more traditional techniques.

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