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Microscopical characterization of carbon materials derived from coal and petroleum and their interaction phenomena in making steel electrodes, anodes and cathode blocks for the microscopy of carbon materials working group of the ICCP

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Abstract

This paper describes the evaluation of petrographic textures representing the structural organization of the organic matter derived from coal and petroleum and their interaction phenomena in the making of steel electrodes, anodes and cathode blocks.

This work represents the results of the Microscopy of Carbon Materials Working Group in Commission III of the International Committee for Coal and Organic Petrology between the years 2009-2013. The round robin exercises were run on photomicrograph samples. For textural characterization of carbon materials the existing ASTM classification system for metallurgical coke was applied.

These round robin exercises involved 15 active participants from 12 laboratories who were asked to assess the coal and petroleum based carbons and to identify the morphological differences, as optical texture (isotropic/anisotropic), optical type (punctiform, mosaic, fiber, ribbon, domain), and size. Four sets of digital black and white microphotographs comprising 151 photos containing 372 fields of different types of organic matter were examined. Based on the unique ability of carbon to form a wide range of textures, the results showed an increased number of carbon occurrences which have crucial role in the chosen industrial applications.

The statistical method used to evaluate the results was based on the "*raw agreement indices*". It gave a new and original view on the analysts' opinion by not only counting the correct answers, but all of the knowledge and experience of the participants. Comparative analyses of the average values of the level of overall agreement performed by each analyst in the exercises during 2009-2013, showed a great homogeneity in the results, the mean value being 90.36%, with the minimum value of 83% and maximum value of 95%.

Keywords: Carbon Materials, Steel electrodes, Anodes, Cathode Blocks, Round Robin, ICCP

1. Introduction

The Microscopy of Carbon Materials Working Group (CMWG) of Commission III "Industrial Applications of Coal Petrology" of the International Committee for Coal and Organic Petrology (ICCP) was proposed by Cornelia Panaitescu during the 59th Meeting of

the ICCP held in Victoria, Canada (Menéndez, 2007). The initiative was based on the Romanian research experience of more 40 years in the field of carbon materials and carbon products (Panaitescu, 1991; Panaitescu and Predeanu, 1999; Predeanu et al., 2000).

The CMWG started its activity in 2008 at the 60th ICCP Meeting in Oviedo, Spain (Predeanu and Panaitescu, 2008). It is aimed at investigation and discussion of the efficiency of microscopical methods for the study of carbon materials derived from coal and petroleum, with an emphasis on quality control of raw materials, intermediary and final products obtained from different processing technologies.

During the research developed by the CMWG conveners, essentially two phases were identified that clearly influence the carbon materials derived from fossil fuels and their interaction phenomena on making steel electrodes, anodes and cathode blocks. These are: raw material type and quality and the parameters applied during technological processing. The conveners accompanied the four exercises carried out between 2009-2013 by using theoretical considerations to improve the evaluation of the images analyzed during the round robins. The major objective of the CMWG of the ICCP is to emphasize the aspects concerning the application of petrographic research in cases of different manufacturing processes of carbon materials and products, based on the experience of conveners and members of the working groups of Commission III of the ICCP.

The four exercises developed by the CMWG (2009-2013) concentrated on analyzing 372 fields in black and white pictures, and the objectives can be summarized as follows:

- (2009) Identify the petrographic textures representing the structural organization of the organic matter corresponding to solid carbon precursors: coal-tar pitch coke, petroleum coke, calcinated anthracite;
- (2010) Identify the mesophase formation from the isotropic aromatic parent liquid to an anisotropic solid texture (nucleation, coalescing, mesophase coalescing final stage) of coal-tar pitches: binder pitch (type A) and impregnating pitch (type C) which are currently used as matrix precursors of many carbon materials; describe the evolution of optical characteristics of pitches during heating to 480, 500, 800 and 1000 °C and the influence on their preparation within the production industrial steps;
- (2011) Identify morphological differences between the three different samples of steel electrodes used: baked electrodes, re-baked electrodes and graphitized electrodes and the interaction phenomena between calcinated petroleum coke and binders: binder pitch and impregnating pitch;

- (2013) Identify the morphological differences in anode and cathode blocks used in the aluminium industry where the petrographic composition depends on the grain size distribution of the blended solids: petroleum coke, anthracite and the quality of the binding material (pitch).

The criteria proposed for the classification of optical texture appearance that have been presented, discussed and approved at annual ICCP meetings, were according to the classification system for textural components in metallurgical coke of the ASTM 2013, and are listed in Table 1. The criteria used to distinguish between different classes considered both the optical texture, type and size, origin and the porosity development. The results were evaluated on 3 levels: (i) optical texture (isotropic or anisotropic); (ii) optical type and size (punctiform, mosaic, fiber, ribbon, domain); (iii) origin of the inclusions.

2. Preliminary consideration

The following chapters highlight the importance of optical microscopy applied to the research of coal and petroleum derived products and main industrial application.

2.1. Carbon materials properties

The quality of the raw carbon material and its manufacturing processes are directly related to the composition and structure and subsequent technological characteristics. The physical-chemical structure of the products provides the properties needed in the utilization processes. These properties are: chemical inertness, mechanical and thermal strength, thermal and electrical conductivity (resistivity), elasticity, reactivity, light-weight, resistance to aggressive chemicals, and radiation. The research methods used for characterization of coal derived materials (of cokemaking industry-pitch and metallurgical coke) and oil derived materials (of petrochemistry-petroleum coke and oils), involves: elemental analyses, chemical catalytical oxidation, reduction, hydrogenation, infra red (IR) spectroscopy, nuclear magnetic resonance (NMR), electron spin resonance (ESR), X-Ray diffraction, and scanning electron microscopy, etc.

There is a close connection between the carbon materials composition, structure and quality. The quality of the products and their behavior in the utilization processes, as intermediate or end products, depends on the way in which the starting materials are chosen and prepared, and, on the operations carried out in the technological flows. Quality is checked by analyzing certain characteristics in which macro-and microstructure plays an important role.

To achieve structures with desired characteristics, the analysis must be based on the raw and prepared materials, prior to entering the production blends. Together with other physico-chemical methods, petrographic research of the structure and optical texture of raw materials,

contributes to obtaining information needed for both phases of the manufacturing process control, and for characterization of the products for their use (Panaitescu, 1991).

The results from coal petrography on the international level have opened a large area of industrial applications. Previous research offered the opportunity to investigate the properties of coal-tar pitch (Lin et al., 2005; Marsh and Menéndez, 1988; Mendez et al., 2003; Rocha et al., 2007) in relation to mesophase formation (Cheng et al., 2008; Mianowski et al., 2003; Nazem, 1980; Parkash and Berkowitz, 1980; Shui et al., 1998), in obtaining carbon-carbon nanocomposites (Predeanu and Panaitescu, 2010a), to observe and establish structure and texture evolution during thermochemical and mechanical processes (Blanco et al., 2000; Machnikowski et al., 2002; Marsh et al., 1999; Panaitescu and Predeanu, 2010; Perez et al., 2004) corresponding to the specific manufacturing technologies (Queipo et al., 2004; Wagner et al., 1988). These studies include research on different types of coal-tar pitch used as binder and impregnation material, together with their coke structure and texture (Collin and Gemmeke, 1977; Dumitrescu et al., 1987; Kvam and Schreiner 2000; Marsh, 1997; Zander, 2000; Mochida and Amamotu, 1977; Mochida and Shiamomura, 1984; Panaitescu, 1991).

2.1.1. Coal derived products

Coal-tar is a complex blend consisting mainly of polycyclic aromatic hydrocarbons, which is commonly distilled to produce chemicals and coal-tar pitch. Both tar and pitch contain resinous components known as toluene insoluble (TI), quinoline insoluble (QI) and beta-resins (coal and coke particles, inorganic compounds), whose content and molecular weight distribution significantly influence the physical properties and, consequently, the upgrading characteristics of the pitch. The quality of crude tar depends on factors (coal quality, coke ovens geometry and parameters, technologies applied for tar separation) which overlap each other (Fig. 1):

- Coking coal (coal origin and type, grain size, moisture, volatile matter, bulk density);
- Coke oven (dimensions, size of free gas collection space, coking temperature and time, temperature in free gas collection space, oven age, charging method, the way the high-pressure exhaustion system is operated);
- Tar separation (methods of separating heavy tar, application of additional separation tanks and tar centrifuges).

The influence of TI and QI is crucial to the quality of coal-tar pitch which is used as binding and impregnating agent in the carbon electrode and refractory industries. A high TI and QI are beneficial in yielding a high carbon residue. However, high TI and QI have negative

effects on the rheological behaviour, and hence on the impregnation properties of pitch (Kandler and Lakata, 1990).

Considering that the amount of solids (TI, QI, and beta-resin) strongly affects the potential utilization of tar and pitches, US Steel Research in 1964 developed a procedure for counting separately the by-product related materials with low ash, the coal-related carbon forms, and minerals. Thus, a microscopic classification of carbon forms in coal-tar and pitch solids was published by Gray and Rhoades (1984).

The quality of graphitizable carbon is directly related to its optical texture which is controlled by the development of mesophase during the carbonization process depending on the reactivity of pitch components. The optical texture is defined by the size, shape and orientation of the different mesophase classification systems, all of them similar and based on the same widely used criteria (Forrest and Marsh, 1982; Forrest et al., 1984; Panaitescu, 1991).

Pitch can be considered an ideal precursor of carbon materials because of its carbon content, very low amount of inorganic compounds, and its capability to graphitize when heated above 2500 °C. A wide range of carbon materials of very different structure and properties can be obtained from pitch of different specifications or even from the same pitch when different carbonization conditions are applied (heating rate, final temperature, residence time, use of pressure).

Gray and Krupinski (1997) developed a microscope classification system, in which the amounts and kind-of carbon forms are determined based on six categories (needle coke, irregular textures, circular or shot, mixed textures, very fine textured, amorphous) and two microstructures (dense sponge and porous sponge). Other papers showed optical micrographs of a variety of carbons obtained from different coal-tar pitches and of a pitch system at different carbonization stages (Menéndez et al., 1997, 2000; Panaitescu and Predeanu, 1999, 2007).

2.1.2. Petroleum derived products

The carbon products industry, specifically electrodes, uses coke obtained from carbonization residue of the thermal treatment of petroleum fractions distillation, cracking, pyrolysis. Petroleum coke is a carbonization product (through the fluidized or delayed coking process of pitch residues of high-boiling hydrocarbon fractions at about 475°C) obtained from petroleum processing. Depending on the supply source, expressed by the chemical nature and manufacturing technology, the coke may be assigned to certain predominate structural types,

which will influence the optical texture characteristics of the electrode structure and its behavior in subsequent thermal processes (Panaitescu, 1991).

Calcination technology is responsible for the specific stress distribution in coke, according to the heat treatment model, and varies with a specific thermal expansion coefficient, the value of which is important for the quality of graphitized electrode. Petroleum coke is calcinated at high temperatures (1200-1400 °C) usually in a gas heated rotary kiln for moisture and volatile removal, in order to increase coke density, strength and electric conductivity. In the thermal processes of calcination and baking, the petroleum coke behaves differently, forming carbons with different graphitization properties. Within the anisotropic structures, graphitability varies with the size and shape of oriented molecular units (their planarity), the larger needle fiber and floral structures being the easiest graphitized. Petroleum cokes used in making carbon artifacts are obtained in delayed (semi-continuous) and fluid (continuous) coking processes. The physical and chemical properties of delayed and fluidisation coke are different, including microscopic characteristics with particular emphases on size and shape and completeness of the unit. The microtexture of delayed petroleum coke varies from needle like to spongy-anisotropic coke to amorphous coke, depending on the nature of the raw oil and the carbonization conditions. The microstructure of fluidization petroleum coke has a characteristic onion ring layering, the microtexture has more amorphous carbon and the optically anisotropic carbons have smaller domains than those in the delayed coke (Gray and Krupinsky, 1997). The experience gained by the CMWG conveners after the use of microscopic methods for the investigation of carbon materials and products in the last 40 years must be mentioned. They obtained valuable information on different industrial production steps, allowing the possibility of improving the technologies and enhance the performance of carbon products (Braga et al., 2009; Dumitrescu et al., 1987; Geagulea et al., 1984; Panaitescu, 1991; Panaitescu and Predeanu, 1997; 1999; Predeanu et al., 2000).

2.2. Carbon materials applications

Worldwide, the number of the carbon forms which are used in different industries is rather high, most of them being derived from fossil fuels: raw and auxiliary materials from petrochemistry (petroleum coke and oils), coke-making industry (pitch and metallurgical coke), and mining industry (anthracite). On the international and national level, the carbon materials industry includes a wide number of amorphous products that are baked and graphitized with various uses in different industries: steel electrodes, chlorosodic electrodes, cathode blocks and anodes for the aluminium industry, Söderberg paste, carbon blocks and refractory for the blast furnaces fuel cells, isolating carbon materials, graphite brushes,

nuclear graphite, carbon fibres, etc (Delhaes, 2013; Marsh and Rodríguez-Reinoso, 2000). The quality of these products must answer to some complex thermo-chemical, mechanical, and electrical stresses, having an increased degree of corrosion and irradiation in different environments.

The main industries using carbon products, steel and aluminium making industries, lie between some important economical and strategic sectors. The production of specialty steel uses electrodes which can transport electrical (thermal) energy into crucibles, Fig. 2. The aluminium industry, the biggest carbon user at present, utilizes anodes to supply electrical energy into the cell of electrolysis by reduction of alumina, Fig. 3. The common technological production flow of steel electrodes and anodes involve obtaining a green (crude or raw) mixture by the use of petroleum coke and binder. For the manufacturing of graphite electrodes, the petroleum coke (80% wt.) is of premium quality, called needle coke, and the binder pitch of about 20% wt. The green mix follows the compression moulding process in which green electrodes are formed, depending on the intended application. The electrode is formed by extrusion which is then baked at almost 850 °C. In some cases the baked electrodes are impregnated with pitch and re-baked to increase their density. During baking the binder pitch turns into pitch coke. The electrodes are further heated at about 3000°C to form graphite. The result is a structure that is completely carbon-bound and contains both non-graphitic carbon and graphitic carbon. This structure is extremely strong in compression and will not creep under load. After graphitization, the electrodes are turned into their final form by mechanical processing. In the electric-arc furnace, the electrodes are joined by connecting pins, called “nipples” (Panaitescu and Predeanu, 2010; Redmount and Heintz, 1997). For anodes, the petroleum coke is mixed with an amount of 15% wt. pitch, and carbon residues in the form of electrographyte (Marsh and Rodríguez -Reinoso, 2000; Marsh et al., 1997; Panaitescu, 1991; Panaitescu and Predeanu, 2010). For cathod blocks, the composition is mainly of graphitized petroleum coke, pitch coke and anthracite, the quality of which (inertinite content, pyrocarbon, minerals, degree of cracking, grain size) is crucial to the finished product characteristics (Fig. 4).

3. Materials and methods

3. 1. Selection of samples

Samples were provided from the industrial flow of SC Electrocarbon SA Slatina, the Romanian manufacturer of graphite electrodes and nipples, calcinated petroleum coke, Söderberg paste and carbon blocks for blast furnaces. In order to collect the necessary data to answer the questions outlined in the aims of the CMWG, four sets of samples were analyzed

during 2009-2013. To check the applicability of the qualifying system for a wide range of carbon materials, samples were selected to cover both raw materials of different organic matter (petroleum coke, pitch cokes, anthracite), intermediary (baked and re-baked electrodes) and final carbon products (graphitized electrodes, anodes and cathode blocks) obtained from the manufacturing industrial flow. Details of origins of sample and types are presented in Table 2 and their characteristics in Tables 3 and 4.

3.2. Sample preparation

Two procedures were adopted for sample preparation:

- I. Solid carbon precursors (samples from the 1st and 2nd set) were ground to <1mm size and embedded in epoxy resin, following ISO 7404-2 (1994). Two parallel mounts in resin with a section close to 2x2 cm, vertical surface x were prepared for each sample and were polished.
- II. Carbon products (samples from the 3rd and 4th set) representing whole-bulk samples were taken from the steel electrodes, anodes and cathode blocks.

For each of the electrodes (baked, re-baked and graphitized) samples of 200x40x15 mm were taken on cross section (400 mm diameter) (Fig. 5). Each of the three lengths was divided into five small pieces of 40x40x15 mm each, numbered as 1-5B (baked), 1-5R (re-baked), 1-5G (graphitized) (Fig. 6, A-C).

Three pieces from the anodes on cross section (50 mm diameter) as in Fig. 7 and four pieces of 50x50x20 mm were cut from the cathode block having a non-regular size, as seen in Fig. 8.

3.3. Sample polishing

The particulate blocks were ground down using progressively finer wet carborundum papers; the final grind was 1200 wet paper; final polishing of the pellets was done using colloidal suspension of aluminium oxide or diamond powder of 3.00 μm and <1.00 μm grain size. Polishing lasted longer for the 3rd and 4th sets, due to the increasing strength of materials determined by the higher structural orientation of carbon in the heat-treated samples.

3.4. Proposed analytical procedure

Following the experience of other Working Groups of the ICCP that had better results on pictures than on real embedded samples. The 372 fields on 151 pictures were selected from a library of over 1400 digital microphotographs. An Olympus optical microscope from University Politehnica Bucharest, with 50x and 20x oil objectives, equipped with a 12 V, 100

W halogen lamp, polarizer, analyzer rotatable through 360° and a Vosskühler VDS 1300 monochrome camera, was used for image collection.

Depending on the analyzed textures, the participants were asked to classify: one or more zones marked by a square (with various possible shapes but with the same morphological type, shape, size), or a point of the intersection threads. The procedure essentially followed those used in other Working Groups of the ICCP: Coke Petrography (see www.iccop.org), Identification and Petrographic Classification of Components in Fly Ashes (Suárez-Ruiz et al., 2008) and Combustion (Lester et al., 2010).

The description of the optical textures was enclosed in a set of examples in order to allow better identification and performance of the exercise. Taking into account the provisions of the ASTM, a synthesized scheme was given to the participants as an XL spreadsheet for their individual readings. A simple classification scheme was used in which the criteria to distinguish between different classes considered both the optical type (isotropic/anisotropic), texture and size. The system had 15 different classes that covered all the possible texture occurrences. A non-compulsory requirement was to identify the origin of certain types of textures (Table 5).

3.5. Statistical analysis

Microscopical evaluation of carbon materials is a relatively difficult task. It corroborates knowledge, in addition to classical notions of coal and coke petrology and information on the intermediate stages in which they occur under certain conditions of temperature and, depending on the proportion of production prescriptions/charges, of information on their association and compatibility in blends.

The main objective of the exercises was to see if the participants identified similar amounts of excellent, good, or low texture quality of the particles in a given sample.

With the questionnaires (XL tables), simply counting correct answers does not fully evaluate analysts' knowledge because it does not take into account the information that the analysts did not check corresponding to a positive identification. This made it necessary to use a method that not only counts the correct answers, but also assesses all of the knowledge held by the analyst.

The goal of the performed assessment was to evaluate how frequently each analyst identifies a structure after studying a number of samples.

It is common, in many fields, to study agreement among ratings of multiple experts using categorical ratings. The main types of categorical ratings are dichotomous (Yes/No, Present/Absent, etc.), ordered categorically (Low, Medium, High, etc.), and nominal

(Isotropic, Punctiform, etc). This study used dichotomous ratings (Yes/No) considering that if the analyst were not to check a space, a negative identification of the structure would be given.

In general, considering the answers of two analysts, we can have these situations:

- both analysts identify the structure and, in this case there is a positive agreement;
- both analysts answered that the structure is not the type that is the subject of the question and, in this case, there is a negative agreement;
- analysts have different opinions and, in this case, there is disagreement.

For assessment of agreement level between two analysts a raw agreement indices, namely the “*level of overall agreement*” was used (Uebersax, 2001).

The level of overall agreement (LOA) is defined as the percentage in which analysts agree, without distinguishing between positive and negative agreement. That is given by the equation:

$$p_o = a + d / a + b + c + d = a + d / N$$

where:

- a, is the number of positive agreement;
- d, is the number of negative agreement;
- b, and c are the numbers of disagreement.

LOA considers both the correct identified answers (positive identification) as well as lack of response, but identified and not marked (negative identification), as well as incorrect responses (disagreement). The LOA gives a broader knowledge that is more accurate (e.g., evaluates also, what the analyst not marked).

This type of method offers the possibility of having a comprehensive assessment of the analyst’s knowledge, by also taking into account the situations when there is negative agreement.

Practically, for the question *Which type of texture is this?* there are two possible answers:

- i) I think this is anisotropic-type structure /yes (and mark the box) or
- ii) I think this is not isotropic-type structure /no (and never mark anything).

There are two more options (of disagreement), but here only of the agreement is discussing:

- (i) The structure was identified as being anisotropic-type both by convener and analyst, so it is considered a positive response i.e. a case of positive identification (positive agreement).

- (ii) The structure was not identified as being isotropic-type both by convener and analyst, so was given a negative answer, i.e. a case of negative identification (negative agreement)

The study considered two cases of agreement (positive and negative). Basically, positive agreement accounts for information which was revealed by the presence of a correct answer and negative agreement default information was caused by negative identification (absence of response). After examining all samples an LOA for each type of structure can be calculated (i.e. anisotropically).

4. Results and Discussion

A range of factors can be considered primarily responsible for the quality evaluation of the results: i) Observation conditions which were, in large part, influenced by magnification and size of the measuring areas selected for assessment; ii) Polish of the samples which determined quality of the images provided to the participants (a very important issue in the assignment of the proposed textures).

4.1. Optical type of the analyzed samples

Overall, 15 participants performed the four exercises on carbon material photomicrograph samples. The analyst numbering in the results evaluation are not related to the ordering of authors in this paper.

Given the need for a gradual identification of the type of structures, firstly of their basic individual forms and secondly, as components of the blends, the conveners considered and developed the activities of the CMWG on two different phases of identification:

- i) Solid carbon precursors: as individual raw materials used in technological processes (2009- Structural organization of the organic matter corresponding to solid carbon precursors: pitch coke, petroleum coke, anthracite; 2010- Identify the mesophase formation from the isotropic aromatic parent liquid to an anisotropic solid texture of two coal-tar pitches);
- ii) Carbon products: as components of various carbon blends (2011-on different steel electrodes manufacturing flow; 2013-on different products anodes/cathodes).

4.2. Solid carbon precursors

Calcinated petroleum cokes physical-chemical characteristics appear in Table 2 and some microtextures of the first CMWG round robin are shown in Fig. 9 (Predeanu and Panaitescu, 2009).

The study of the optical texture of the two needle petroleum cokes shows the optical structure varying from mosaic to needle structures, and the development of the anisotropic texture.

Anthracite physical-chemical characteristics are listed in Table 2, and optical textures are shown in Fig. 10, in which different calcinated anthracite grains reflecting the fissuration caused by calcination appear, which vary in shape and size. It is observed that the pyrocarbon appear as buds and skins of different shapes and sizes, with specific structures produced during hydrocarbons cracking at certain heating rates (Fig. 10F). Depending on the amount, pyrocarbon appearance in anthracite calcination brings significant effects to the resistivity and graphitizability.

Binder and impregnating pitches were prepared from the coal-tar pitch and their characteristics appear in Table 3.

To highlight the crucial aspects of pitch behaviour during coking as much as possible, the conveners conducted extensive laboratory experiments to obtain the appropriate informations and provide them to the participants. During the second round robin of the CMWG participants were asked (Predeanu and Panaitescu, 2010b): i) to identify the mesophase formation from isotropic aromatic parent liquid to an anisotropic texture (nucleation, coalescing, mesophase coalescing final stage); ii) to classify the optical appearance during thermal evolution of the coal-tar pitch carbon textures following the scheme of ASTM D5061-92 (2013).

The development of mesophase during the carbonization process followed the conditions of Table 2, and the optical textures presented in Fig. 11.

The first task chosen was to identify the formation of anisotropic coal-tar pitch mesophase from the isotropic phase during heating. The optical texture of experimental binder and impregnating pitch was defined by the size, shape, and orientation of the different mesophase spheres corresponding to different carbonization stages: nucleation (embryonic stage), growing, and coalescing (Fig. 11A-D). Mesophase spheres appeared to have distinct textures and mainly medium and coarse sizes. The contrasting areas in the textures (anisotropy) corresponded to those where the liquid crystal molecules were oriented in different directions. Early conversion of coal-tar pitch to semicoke takes place with increased heat treatment. The mesophase spheres coalesced to an incipient structural organization before solidification to semicoke (Fig. 11E,F). The final stage of conversion to semicoke takes place with increased the duration of heat treatment (from 1 to 2 hours) (Fig. 11G-J). The optical texture varied from coarse mosaic to domain and even flow type, depending on the nature of raw coal-tar and the technological parameters of coking.

With continuous heat treatment (at 800 °C and 1000 °C and 1 hour soak time) semicoke resulted from mesophase pitch, developed a higher structural organization to coke with more

reflecting anisotropic units and larger porosity (Fig. 11K-N). The temperatures of 800 °C (type C pitch) and 1000 °C (type A pitch) were used to get the re-baking stage after impregnation and respectively, the baking phase corresponding to the industrial processes (Panaitescu et al., 2010; Predeanu et al., 2010).

4.3. Carbon products

To identify the morphological differences that occurred between the three different samples of steel electrodes, during the third CMWG exercise (Predeanu and Panaitescu, 2011), the conveners used baked electrodes, re-baked electrodes, and graphitized electrodes in order to identify, by microscopical analyses, the interaction phenomena between calcinated petroleum coke: binder pitch (A) and impregnating pitch (C), as seen in Fig. 12.

For the baked electrodes, anisotropic optical texture is defined mainly by the size, shape and orientation of the calcinated petroleum coke and binder pitch coke components (Figure 12 A-F). The results confirmed that for pressed products, baking is necessary to obtain an adequate amount of binder coke and homogeneous structures (no internal cracks, density as uniform as possible). Baking was done by indirect heating of green electrodes, at temperatures of about 1000 – 1050 °C, during cycle duration of about 700 hours that depended on the type and size of final carbon products. By heat treatment baking, the pitch binder was changed into a stable network. The heating rate was slow and differential (between 0.7-3 °C/min) within the temperature interval. This consolidated the desired shape and size of the final products, and ensured the mechanical strength and a certain range of physical properties of the products.

For the re-baked electrodes, the process was done by filling the pores with impregnating pitch, as much as possible, so that with new baking the pitch turns to coke and thus, the product became denser and stronger. Impregnation is the technological operation applied to some baked carbon products (electrodes, electrode nipples, and chlor-alkali electrodes) in order to reduce the porosity and increase the mechanical strength. The impregnation process is mainly influenced by the properties of the products that are impregnated (porosity, pore size, and type), the quality of the pitch and how the technological operations are carried out.

After impregnation, the carbon products were subject to re-baking with a heating rate that varied between 3.0-11.0 °C/min. Effectiveness of the process can be followed by microscopic research, revealing various aspects of penetration of the pitch into the porous structure of the product, and within the porosity (sometimes quite high) of the petroleum coke. The re-baked electrodes show an anisotropic optical texture which is defined mainly by the size, shape and orientation of the carbon components, petroleum coke, and impregnating pitch coke (Fig. 12G-I). Depending on the pitch characteristics, as well as the impregnation efficiency and re-

baking conditions, the aspect of the pores filled by pitch coke, clearly show that the manufacturing technology can be monitored by petrographic research (Predeanu et al., 2013). For the graphitized electrode types, heat treatment was applied after re-baking, to change the structure of amorphous carbon into a crystalline structure and to obtain products with properties similar to those of graphite (high electrical and thermal conductivity, decreased hardness, and ease of mechanical processing).

The change of the properties of carbon products during graphitization begins at temperatures of about 1500 °C up to 2200 °C and up to the limit of graphitization at 2500-3000 °C. To obtain a high quality of graphitized carbon products (no cracks, dense), the heating rate was limited to a maximum of 30 °C/h-50 °C/h depending on the heating interval. The decreased porosity in graphitized electrodes results from decreasing crystalline structure as well as from advanced contraction.

Microscopic appearance of these structures is less varied than of the baked and re-baked electrodes, because of uniform high temperature heating. This structural uniformity is characterized by decreased optical crystallinity, increased density of the solid and the disappearance of large surface anisotropy. Optical texture and orientation of the original carbon components (such as the petroleum coke and pitch cokes in Fig. 12J-L) are difficult to be evaluated in graphitized electrodes.

For anodes, technological production are similar to steel electrodes, and involve the obtaining of a green mixture by the use of petroleum coke and binder pitch, as presented in Fig. 3. The nature and thermal treatment of pitch leads to variable coke structures and binding characteristics.

For cathode blocks, the compositions are mostly similar to graphitized petroleum coke, binder pitch and anthracite (Fig. 4), which contain inertinite, pyrocarbon, minerals, cracks, and different grain size, which is crucial to the finished product characteristics.

Petrographic composition of anode (Fig. 13A-F) and cathode blocks (Fig.13G-L) were evaluated during the fourth exercise of the CMWG (Predeanu and Panaitescu, 2014). Morphological differences show that their composition depends on the grain size distribution of the blended solids and the quality of the binding material.

4.4. Evaluation of the results

The method used to evaluate the results is based on the "raw agreement indices" described by Uebersax (2001) and detailed in section 2. The author showed that raw agreement indices are important descriptive statistics, having a unique common-sense.

Comparative analysis of the results is difficult because within each exercise different materials were analyzed and the analysts group structure varied widely (only 3 analysts participated in all exercises). Optical types and forms of the carbon materials identified in each exercise are presented in Tables 6 and 7. For mosaic and fiber types, the values are individual and for the three subtypes (fine, medium and coarse) are averages. The "level of overall agreement" (LOA) for improves for materials that have been studied two consecutive years (i.e., binder pitch and impregnated pitch).

After analyzing the value of LOA for each structure (mosaic and fiber were considered individual values for the three subtypes - fine, medium and coarse), the following conclusions can be drawn:

In 2009:

- For petroleum coke, almost half of the textures had an LOA value between 85% and 95%, and optical types (punctiform and mosaic fine) were identified in about 95% to over 95%;
- For binder pitch, 63.64% of the textures had an LOA value over 85%, and four of them (fiber fine, fiber medium, fiber coarse, and ribbon) were identified with a score of 100% by all analysts;
- For impregnation pitch, all structures were identified with a LOA value of over 75%, and from which half (54.5%) were over 95%.
- For calcinated anthracite, 72.7% of the textures have scores over 95%, for both optical types (isotropic and anisotropic), scores remained under 75%;

In 2010:

- For binder pitch, 90.1% of the textures were identified with LOA values between 85% and 95%. Only one optical type (anisotropic) had scores under 85%;
- For impregnation pitch, over half of the textures had scores between 85%- 95%, three quarters being identified with scores of over 95% (punctiform, fiber fine and fiber medium);

In 2011:

- For baked electrodes, 72.7 % of the textures were identified with an LOA value between 85%-95%, three quarters being identified with scores over 95% (isotropic, punctiform and mosaic fine);
- For re-baked electrodes, about half of the textures (45.5%) had a LOA between 85%-95%, no texture was identified under 75%, and four of them (isotropic, punctiform, mosaic fine, and mosaic medium) had a score of 95%;

- For graphitized electrodes, 36.3% of the textures were identified with an LOA between 85%-95%, anisotropic type being identified with a score under 75% and punctiform, fiber fine, and ribbon, with scores over 95%;

In 2013:

- For anodes, 27.27 % of the textures were identified with an LOA between 85%-95%, mosaic coarse was identified with a score under 75%, and isotropic-type, punctiform and mosaic fine with over 95%;
- For cathode blocks, five textures (punctiform, mosaic fine, medium and coarse and fiber fine) have scores over 95%, 18.1 % were identified with an LOA between 85%-95%, and isotropic and anisotropic types were identified with a score under 75% .

In all studied carbon materials (precursors and products), isotropic texture was identified with the most agreement, with a mean LOA of 87.7%, which of 5.1% represents positive identification and 82.6% negative identification. With optical shape, the best agreement was for identification of punctiform type, with a mean value LOA of 98.1% which of 1.3% represents positive identification and 96.8 % negative identification. Then, followed the agreement for identification of fiber type of 92.3% which of 2.5% represents positive identification and 89.8% negative identification. Anisotropic texture was identified with the most agreement, with a positive identification of 68.05%. Dynamics of average LOA for each type and shape, in each year, appear in Fig. 14a and Fig. 14b.

In Fig. 15 the percent of the LOA obtained by each analyst for the years 2009-2013 is presented. We can observe a high average agreement level (around 90%) for all exercises, with the highest score in 2010 and the lowest score in 2013.

Comparative analyses of the average values of the LOA performed by each analyst in the exercises 2009-2013 are presented in Fig. 16. It shows a great homogeneity of the results, the mean value of the LOA being 90.36%, with the minimum value of 83% and a maximum value of 95%.

5. Conclusions

The main conclusions from the interlaboratory exercises performed by the Microscopy of Carbon Materials Working Group in Commission III of the ICCP, are as follows:

- Microscopical evaluation of carbon materials is a relatively difficult task because it requires classical knowledge and experience about coal and coke petrology along with information about the intermediate stages in which they occur given certain conditions of temperature and, proportion of production prescriptions/charges, with information on their association and compatibility in blends.

- Petrographic textures representing the structural organization of the organic matter derived from coal (calcinated anthracite, binder pitch and impregnation pitch), petroleum (coke), and their interaction phenomena on intermediary processing technologies (backing and re-backing) and final products (graphitized electrodes, anodes and cathode blocks) were evaluated.
- Optical texture characterization of the materials was done using the ASTM classification for textural components in metallurgical coke. The morphological differences were classified as optical texture (isotropic/anisotropic), optical type (punctiform, mosaic, fiber, ribbon, domain) and size.
- The statistical method used to evaluate the results gives a new and original view on the analysts' opinion by not only counting the correct answers, but all knowledge of the participants. Considering correct answers along with the participant's knowledge of the subject matter. The method for evaluating the results, in terms of the "level of overall agreement" (LOA), was well-selected, given the type of evaluation made. Also, for further comparative analysis of the results obtained by application of this method, use of same materials and analyst group is more appropriate.
- Comparative analysis of the average values of LOA performed by each analyst in exercises 2009-2013 shows a great homogeneity of the results, the mean value of LOA being 90.36%, with the minimum value of 83% and a maximum value of 95%.
- Overall, very encouraging results were obtained in determining the morphological differences of samples studied during four round robin exercises. This can be concluded because: conducting four exercises in five years, ensured continuity of the information provided, all analysts appeared to become more confident in identifying carbon forms during the exercise, the accumulated knowledge of the participants from other working groups of the ICCP with certain similar target, took advantage of existing experiences, and good quality of polished samples and of images provided to the participants increased LOA.
- These results suggest optical studies and textural assessment of the effects of structural organization of organic matter derived from coal and petroleum can be applied reproducibly in analyzing technological production processes for steel electrodes, anodes and cathode blocks.

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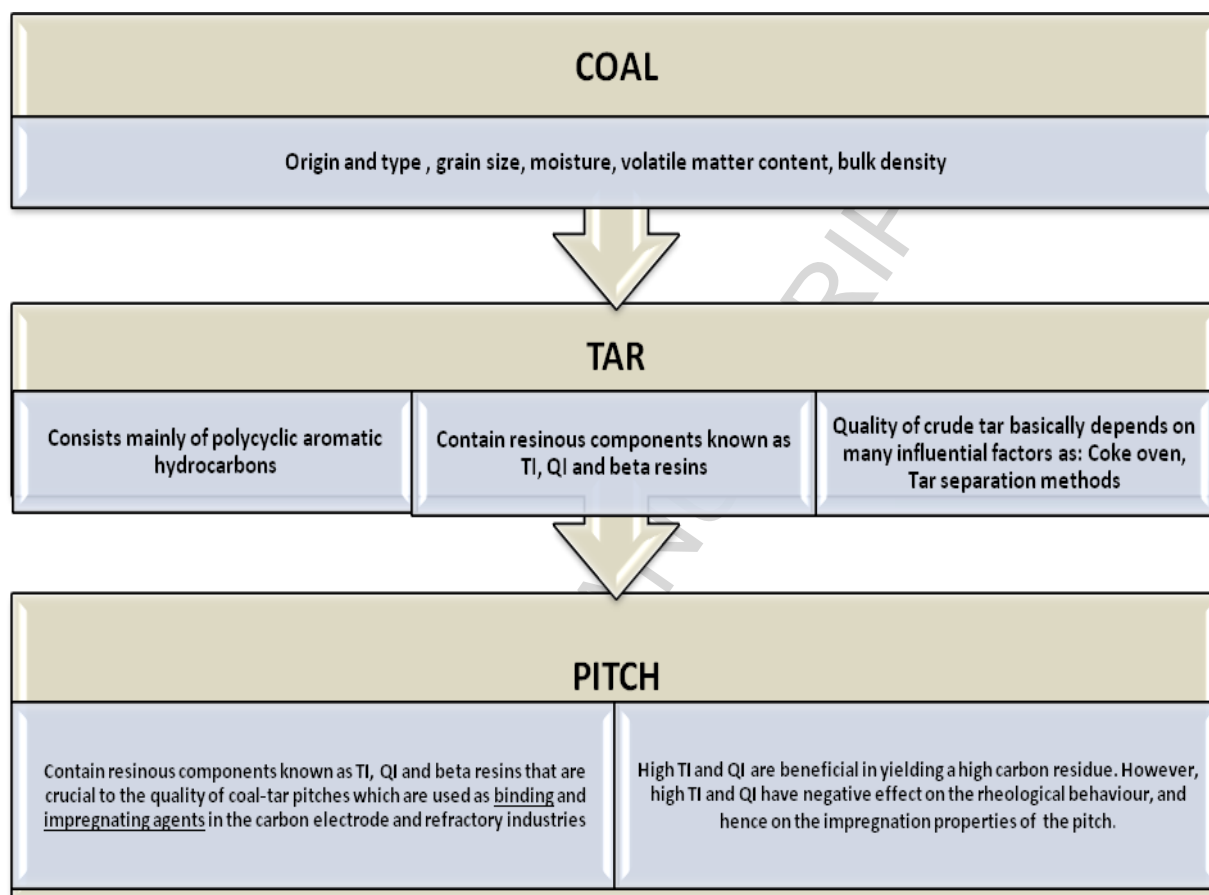
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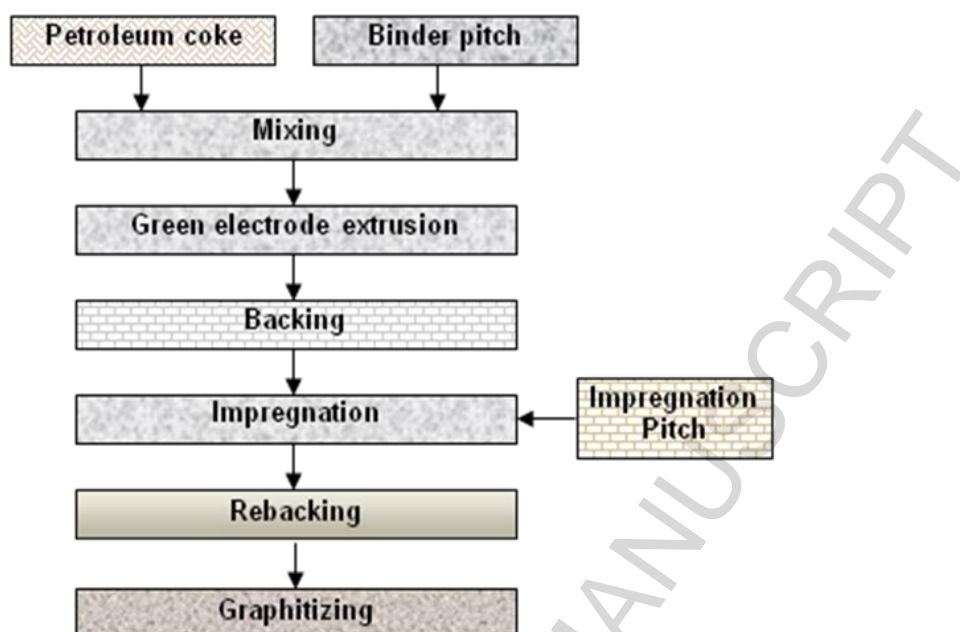
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Fig.1.



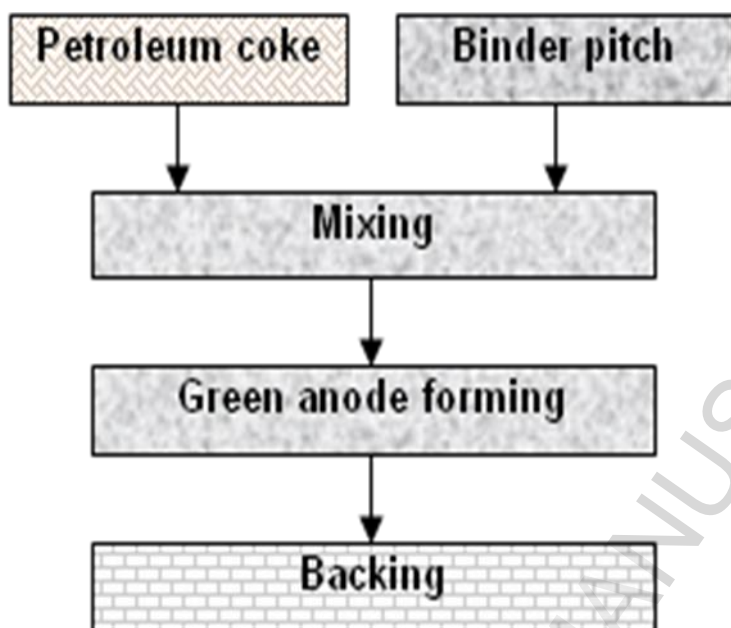
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Fig.2



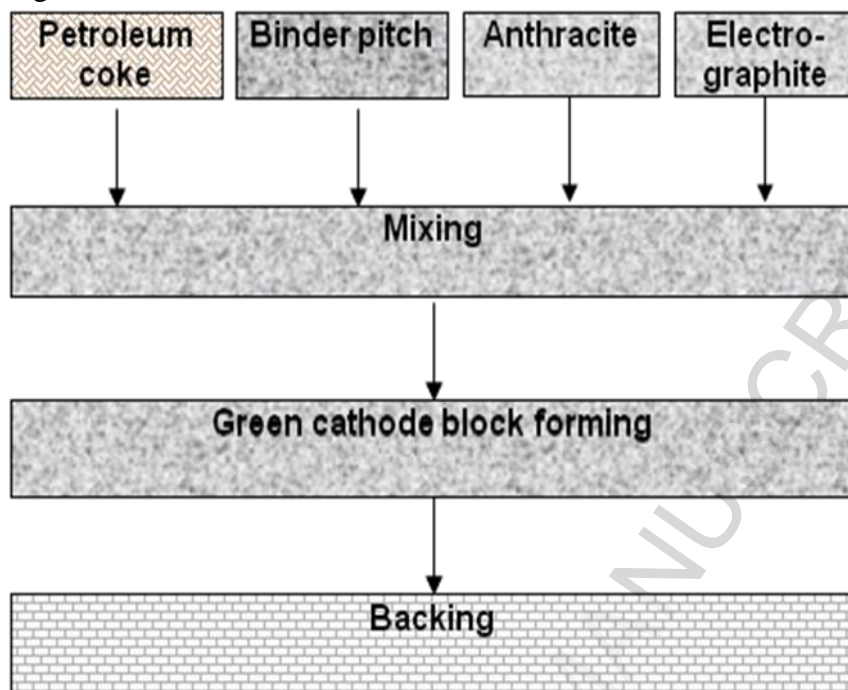
1/13 impregnation pitch instead of pitch
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Fig.3.



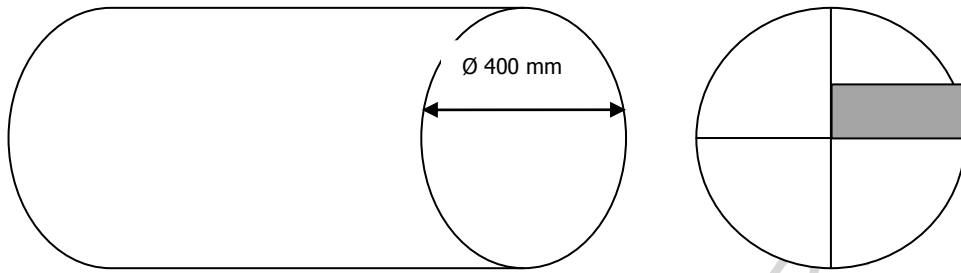
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Fig.4.



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Fig.5.



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Fig.6.

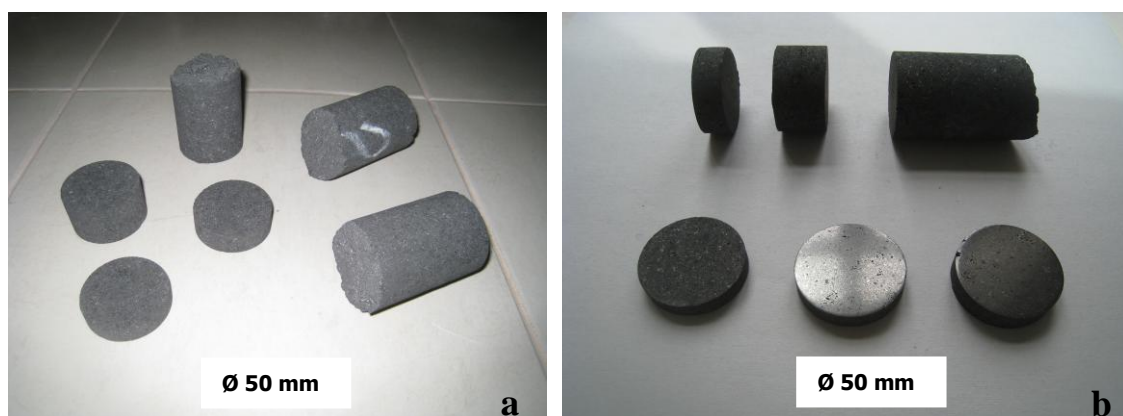


Fig.7

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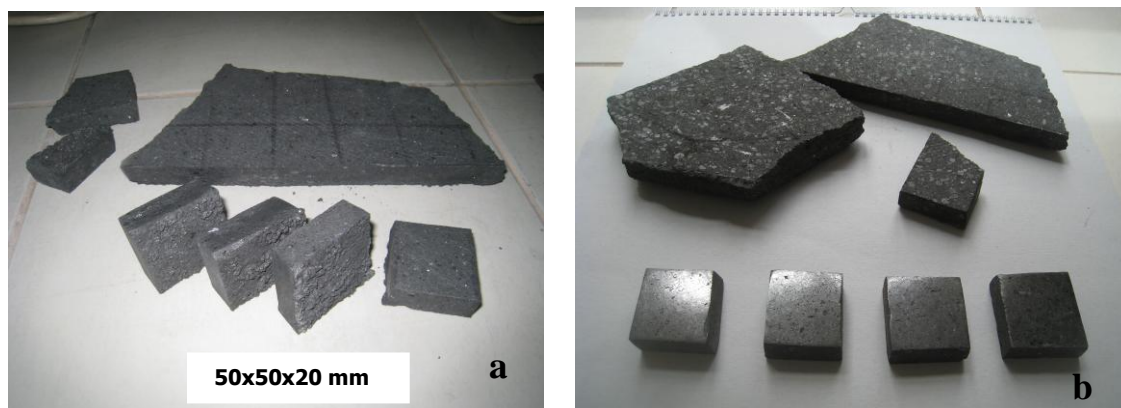
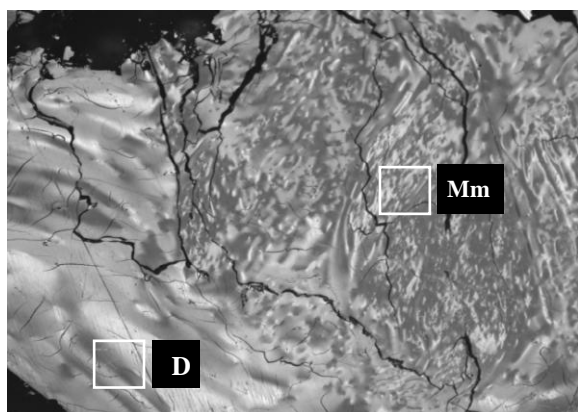
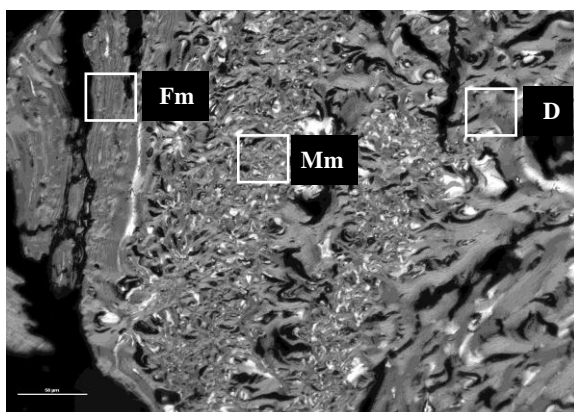


Fig.8.

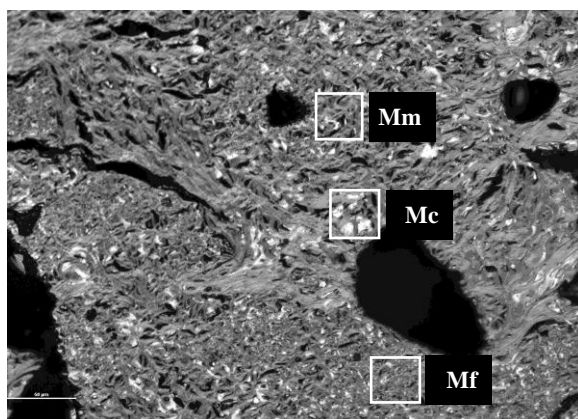
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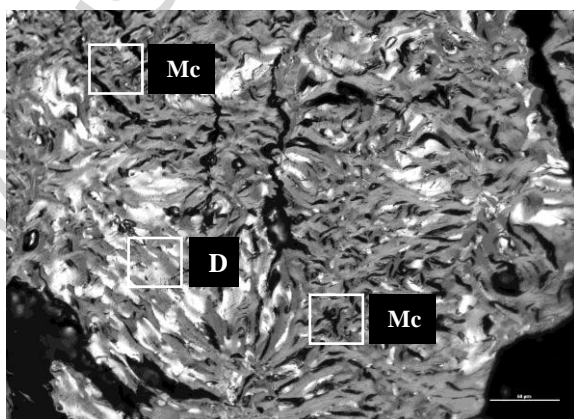
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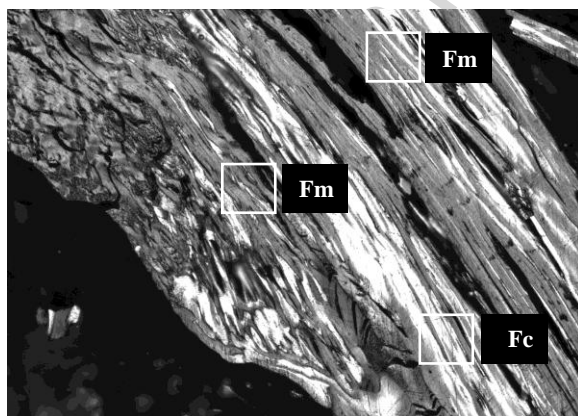
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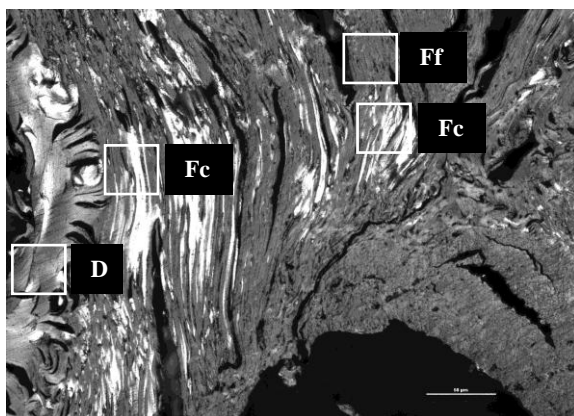
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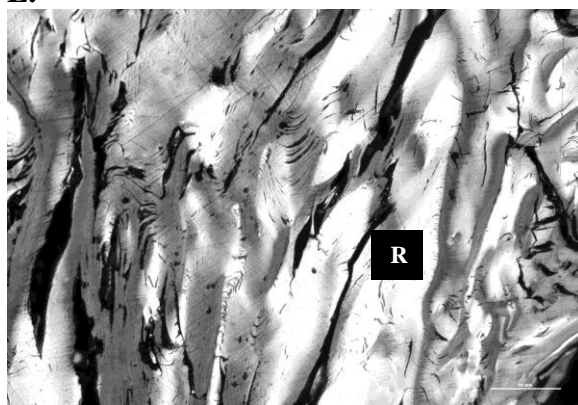
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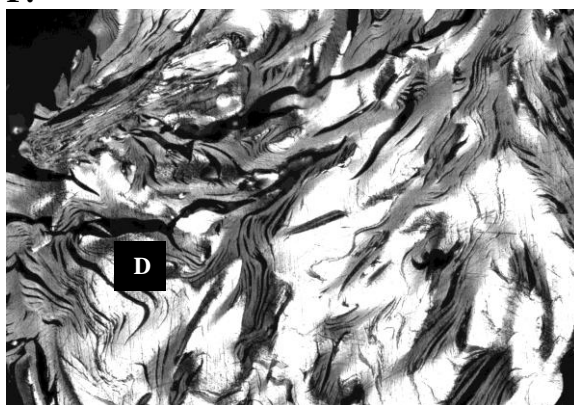
E.



F.



G.



H.

Fig.9

50 μm

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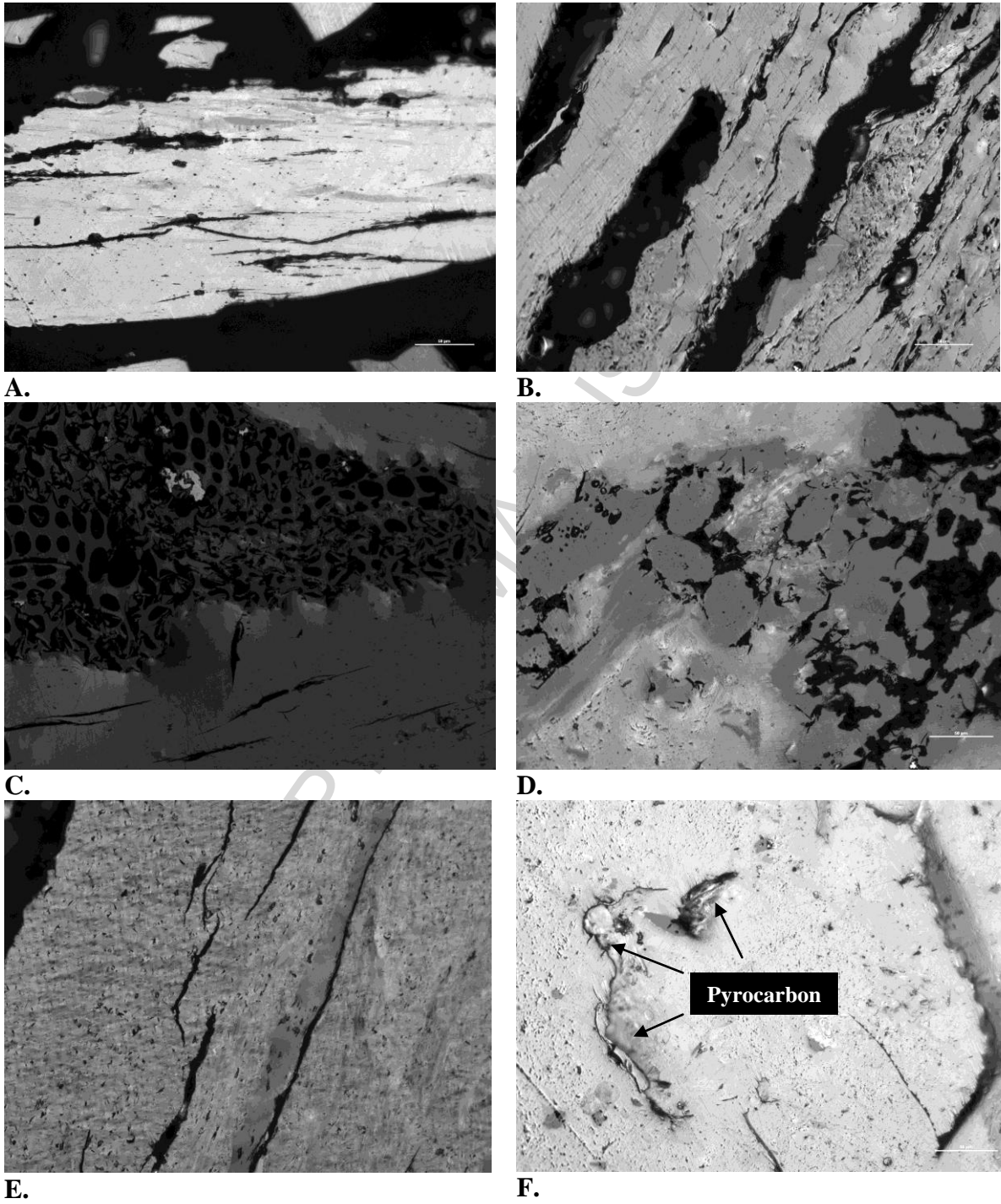
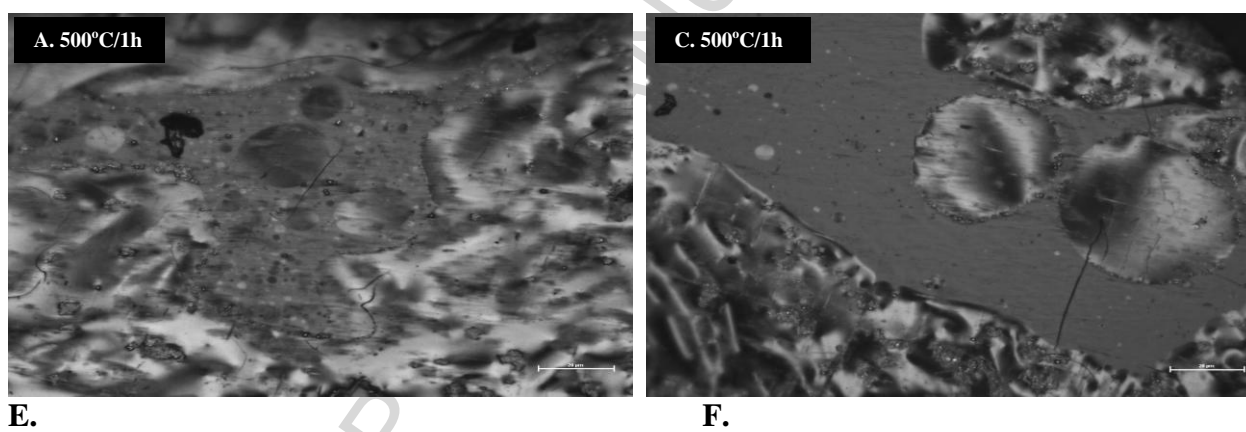
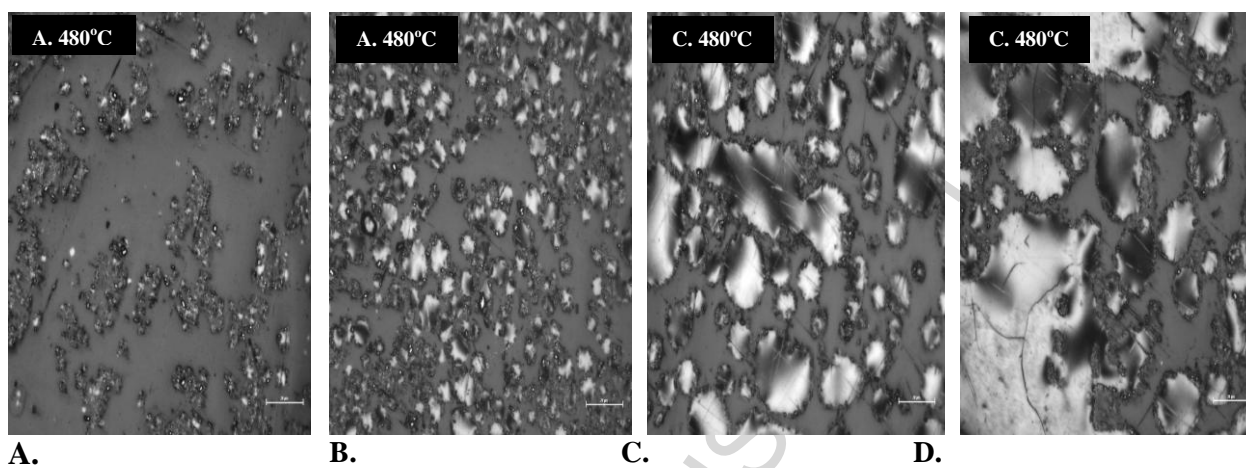
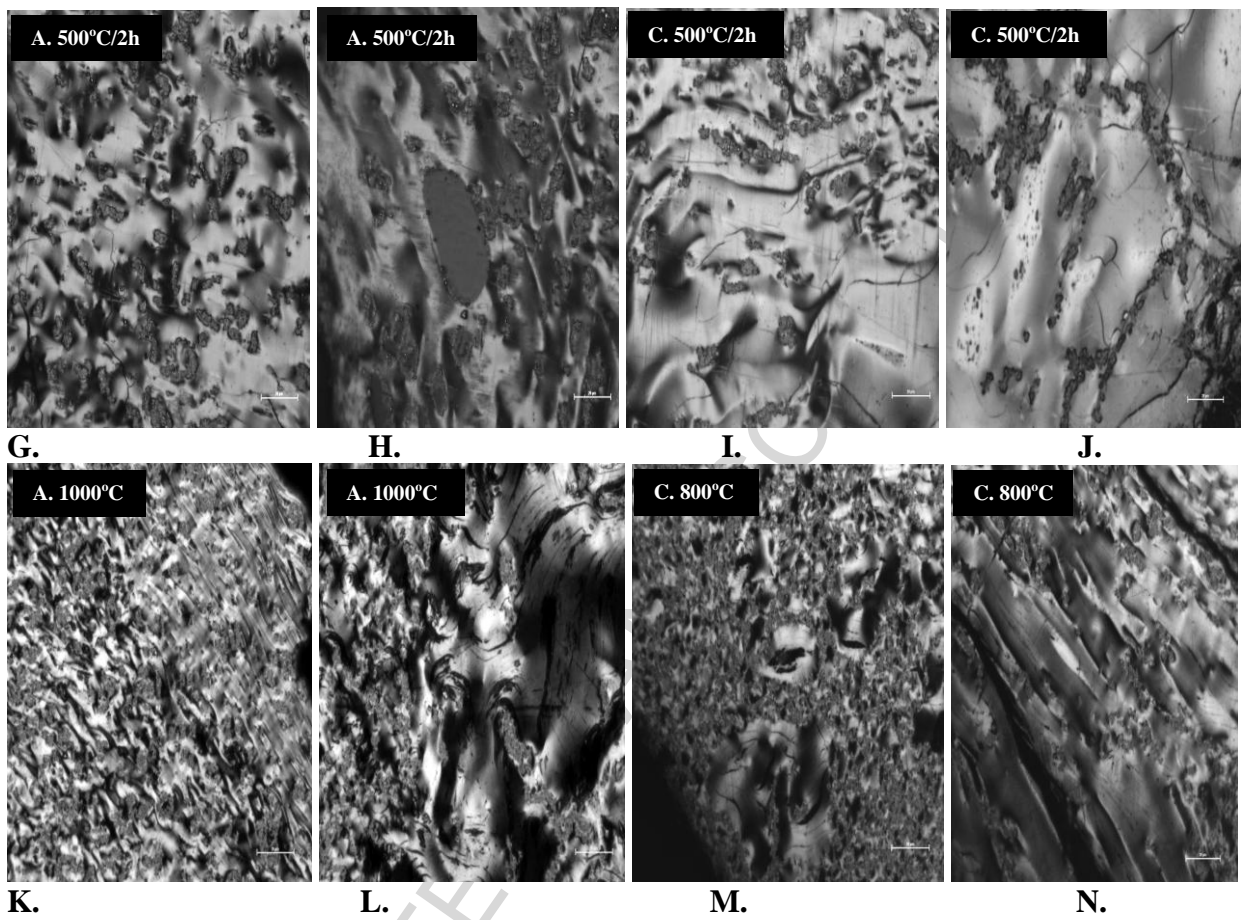


Fig.10



**Fig.11**

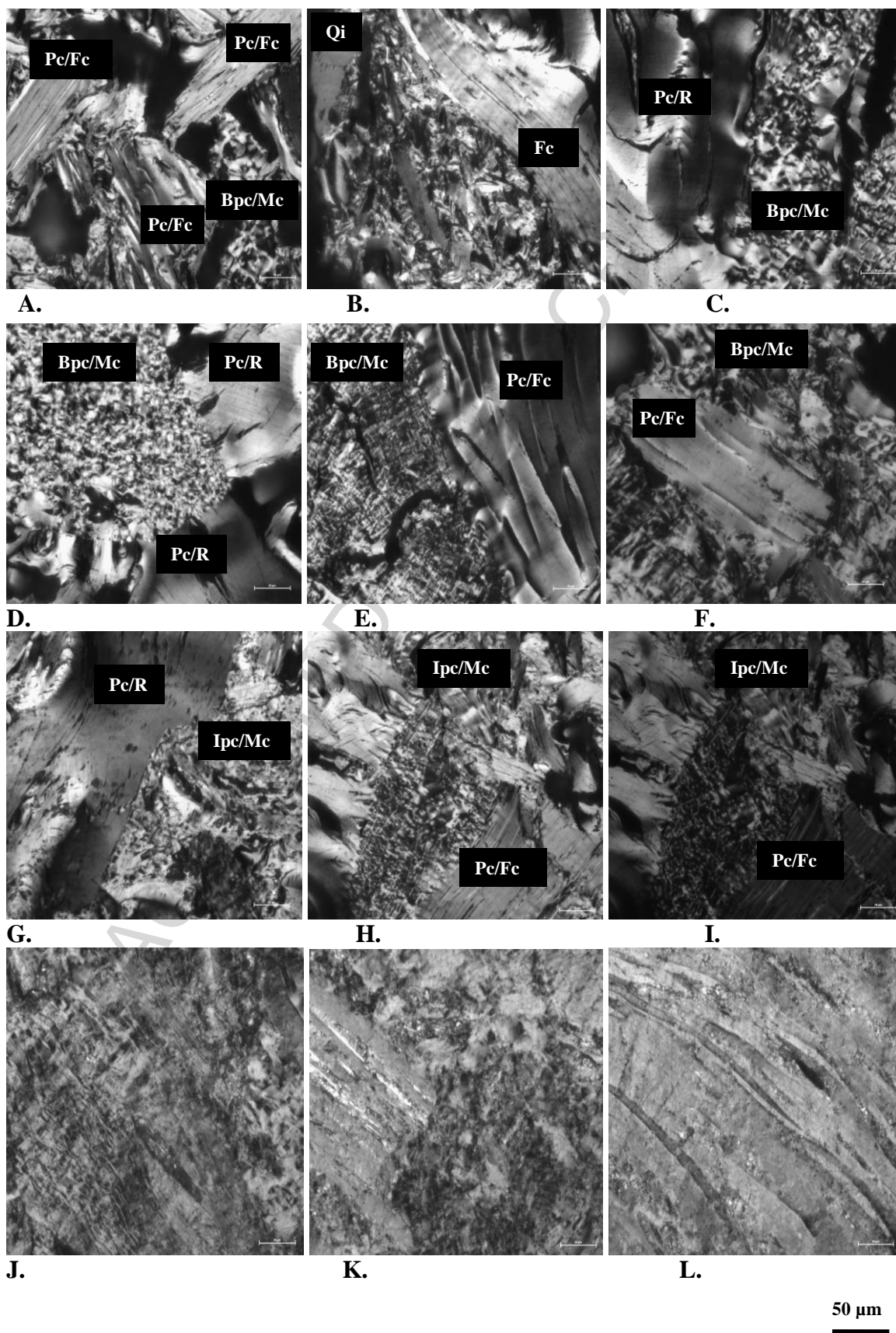
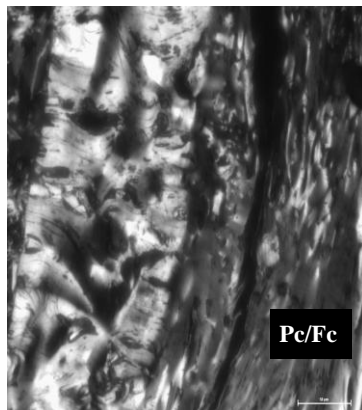
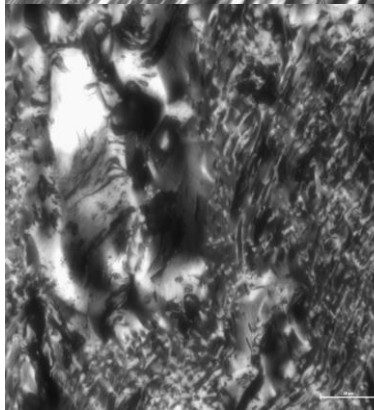
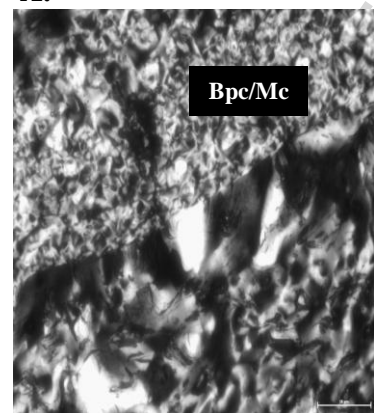
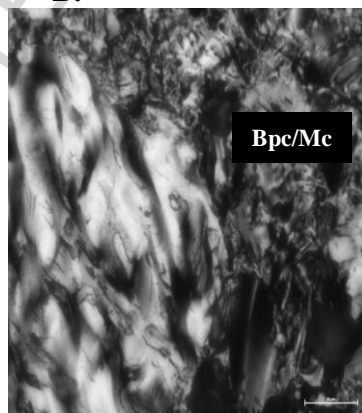
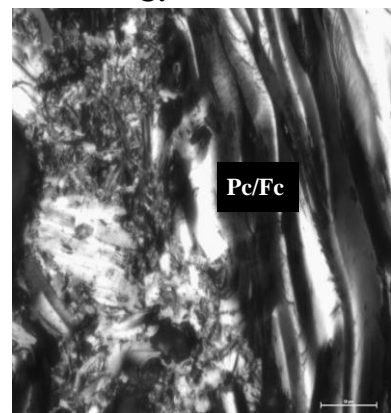
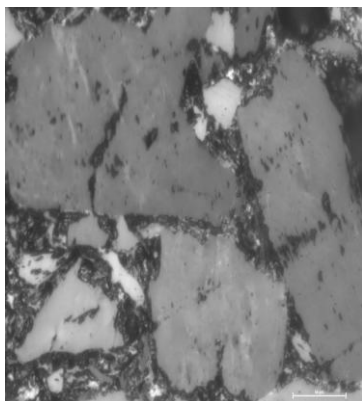
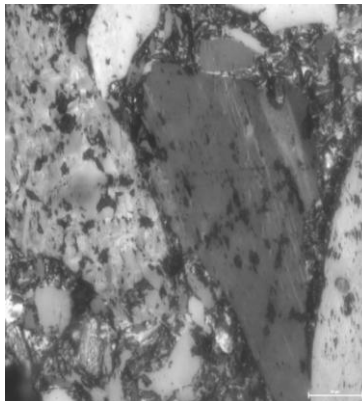
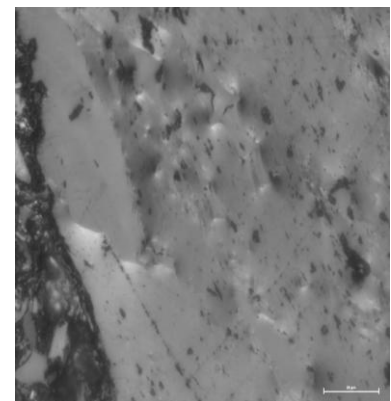


Fig.12

ACCEPTED MANUSCRIPT

**A.****B.****C.****D.****E.****F.****G.****H.****I.**

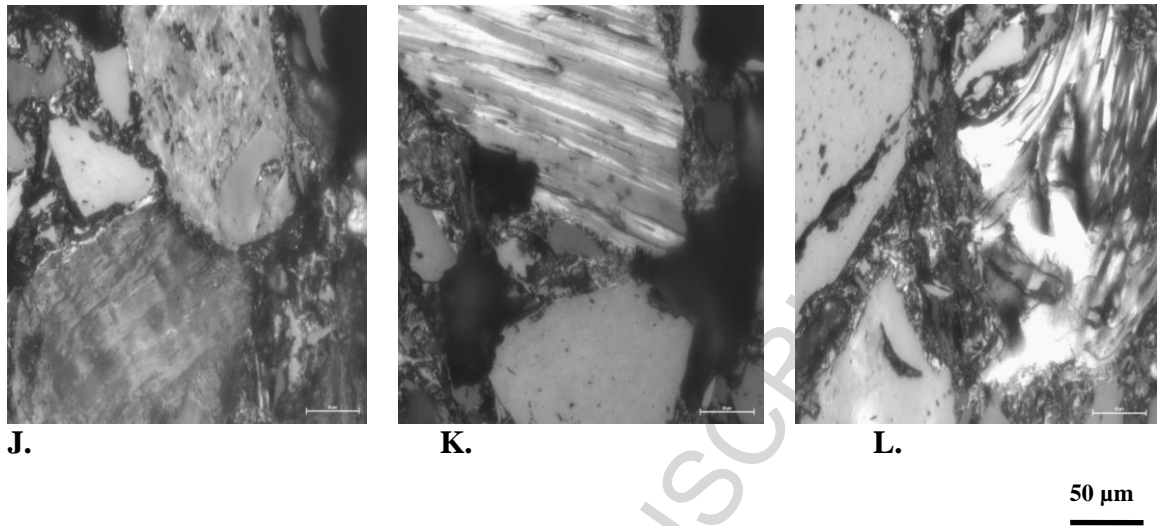
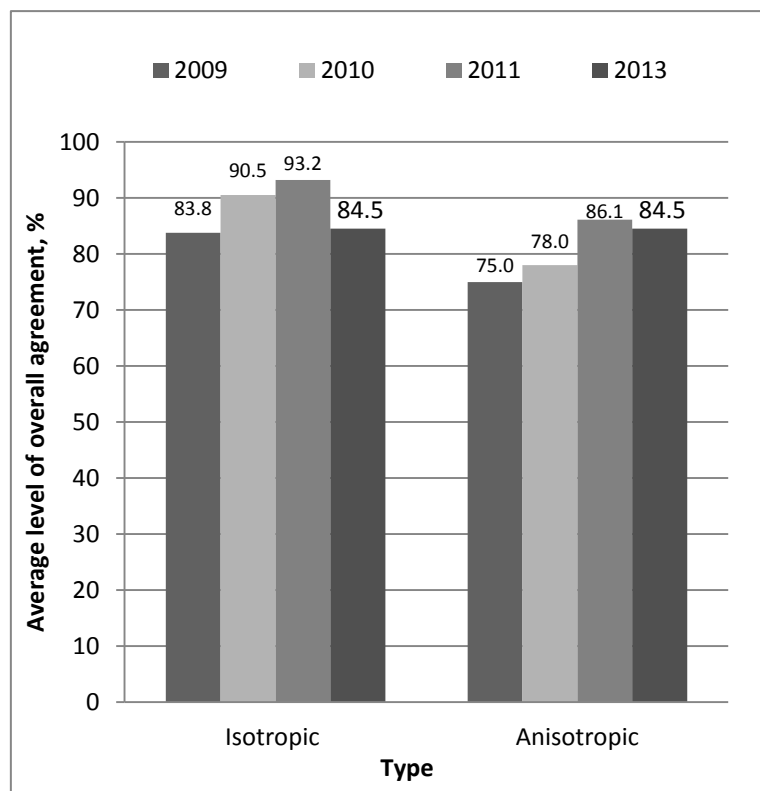
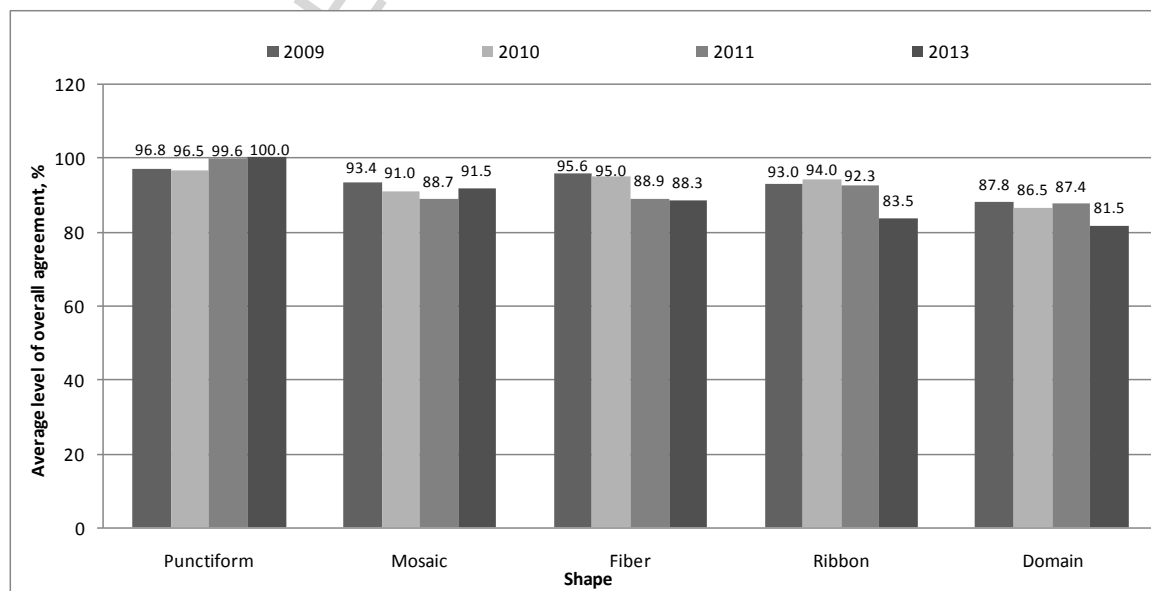


Fig.13

Fig. 14. (a, b)



a



b

Fig. 15.

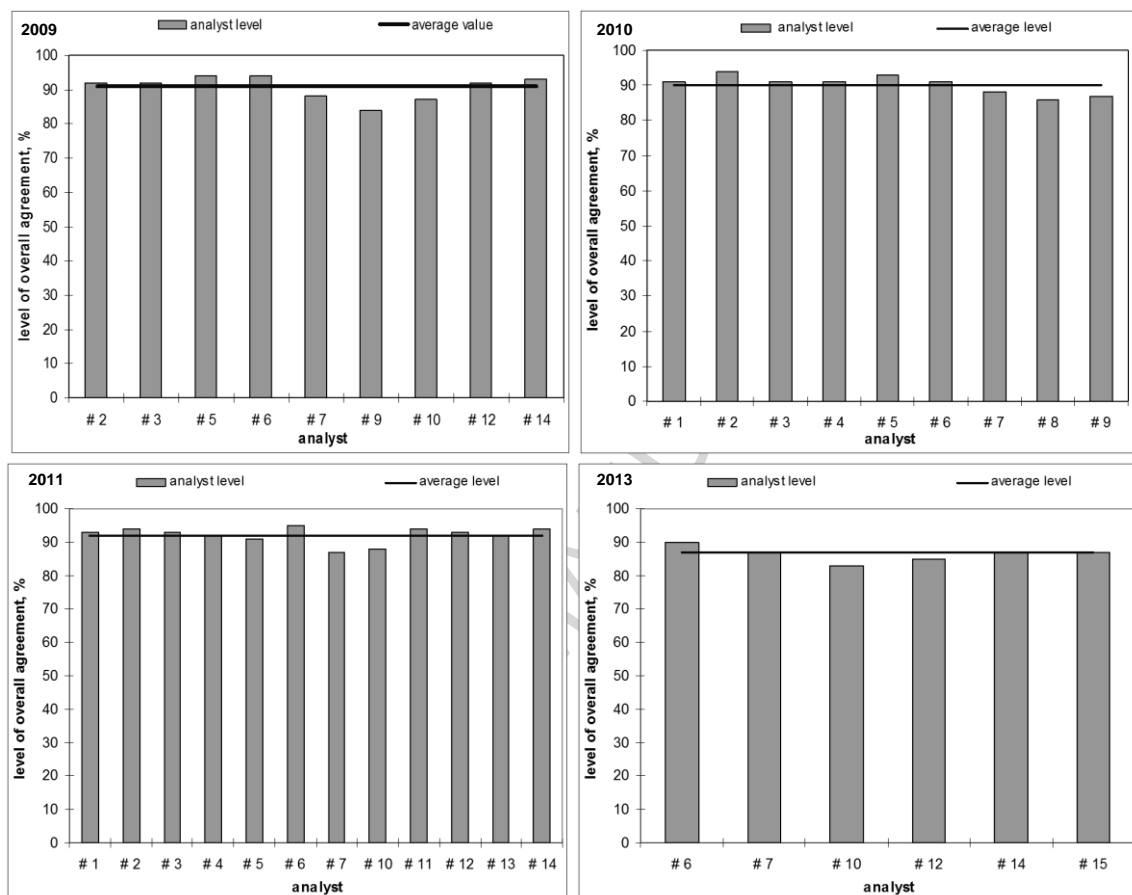


Fig. 16.

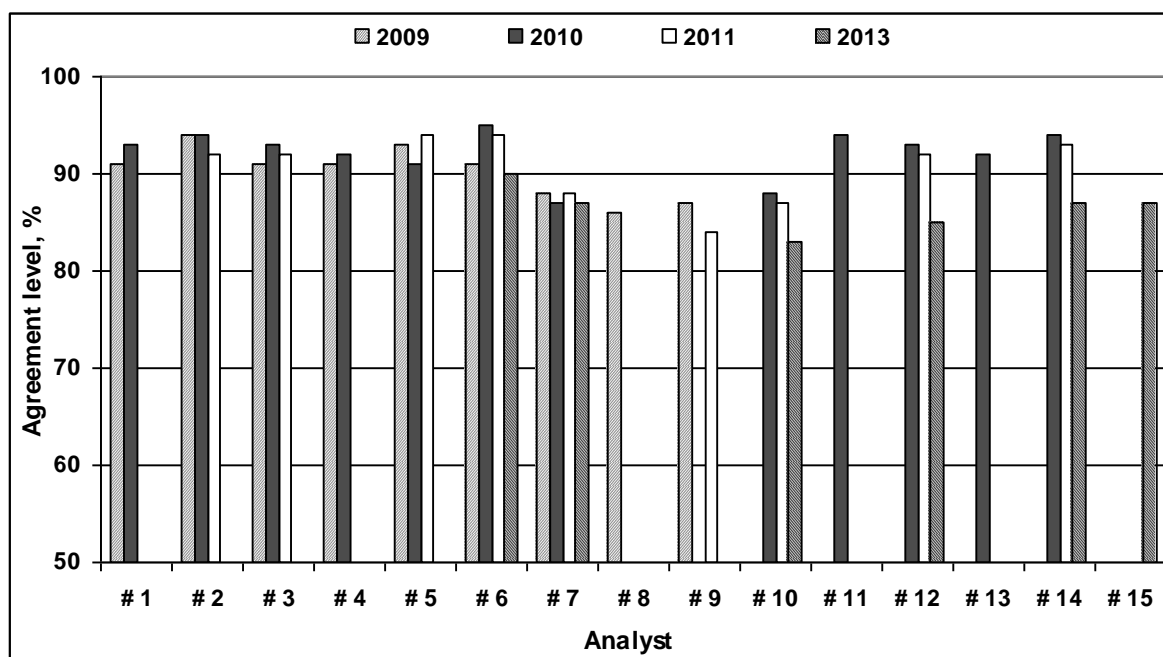


Figure captions

Fig. 1. Factors that influence the quality of coal-tar pitch.

Fig. 2. Industrial production flow of steel electrodes.

Fig. 3. Industrial production flow of the anodes.

Fig. 4. Industrial production flow of the cathode blocks.

Fig. 5. Scheme of sampling the electrodes.

Fig. 6. Steel electrode pellets preparation: (a) rectangular samples taken on the electrode cross section; (b) numbering of the samples from outside (1) to the inside (5) of the electrode; (c) piece samples.

Fig. 7. Anode pellets preparation: (a) sampling on the cross section and (b) piece samples.

Fig. 8. Sampling the cathode blocks (a) and pellets for microscopic analysis (b).

Fig. 9. Examples of different optical textures of petroleum coke in the precursor samples [mosaic coarse (Mc), mosaic medium (Mm), mosaic fine (Mf), fibre coarse (Fc), fibre medium (Fm), fibre fine (Ff), ribbon (R), domain (D)]; PL, imm, 500X: **A**. Green petroleum coke of Brazi; **B, C, D, G**, Brazi calcinated anisotropic coke; **E, F, H**, Conoco calcinated anisotropic coke.

Fig. 10. Aspects of calcinated anthracite, PL, imm, 500X: (A) Vitrinite grain with thin degassing fissures and isotropic inertinite (gray); (B) Vitrinite particle with long degassing fissures and anisotropic semifusinite (gray); (C) Vitrinite particle and isotropic semifusinite (gray); (D) Anisotropic vitrinite particle and isotropic fusinite (gray); (E) Anisotropic semifusinite grain with a slide of vitrinite (middle); (F) Anisotropic vitrinite with pyrocarbon buds and skins.

Fig. 11. Examples of different optical textures of pitches in the precursor samples, PL, imm, 500X: **Binder pitch mesophase optical transformation**: (A) Nucleation (embryonic spheres stage); (B) Spheres growing; (E) Incipient structural organization of mesophase coalescing to semicoke; (G) Mesophase structural organization to semicoke; (H) Isotropic inclusions of insoluble matter in semicoke; (K, L) Optical textures of highly oriented binder pitch coke obtained at 800°C with a variety of textures from mosaic medium to needle like, ribbon and domain type. **Impregnation pitch mesophase optical transformation**: (C, D) Optical transformation of pitch mesophase during growing and coalescing spheres; (F) Pitch mesophase coalescing to semicoke; (I, J) Semicoke optical texture of domain and flow type; (M, N) Optical textures of highly oriented impregnating pitch coke obtained at 1000 °C with textures varying from mosaic medium and coarse to fibre and domain type.

Fig.12. Examples of different optical textures of steel electrodes [mosaic coarse (Mc), mosaic medium (Mm), mosaic fine (Mf), fibre coarse (Fc), fibre medium (Fm), fibre fine (Ff), ribbon (R), domain (D), pet coke (Pc), binder pitch coke (Bpc), impregnation pitch coke (Ipc), quinoline insolubles (Qi)]; PL, imm, 500X: **Backed electrodes:** (A-F) Anisotropic pet coke grains of highly oriented matrix (fibre to domain type) embedded by anisotropic coarse mosaic binder pitch coke with visible inclusions of quinoline insolubles. **Re-backed:** (G-I) Anisotropic pet coke textures well embedded because of the impregnation pitch coke. **Graphitized:** (J-L) Optical texture of graphitized, densified samples of fibre-like and elongated ribbon-type textures.

Fig. 13. Examples of different optical textures of anodes and cathode blocks in the studied samples [mosaic coarse (Mc), mosaic medium (Mm), mosaic fine (Mf), fibre coarse (Fc), fibre medium (Fm), fibre fine (Ff), ribbon (R), domain (D), pet coke (Pc), binder pitch coke (Bpc)]; PL, imm, 500X: **Anodes:** (A-F) Anisotropic optical textures of highly oriented pet coke types and binder. **Cathode blocks:** (G-L) Blended solids (graphitized petroleum coke and calcinated anisotropic anthracite) and binding material.

Fig. 14. Dynamics of average level of overall agreement for the textures optical type (a) and shape (b).

Fig. 15. Comparative evaluation of the results in the 2009-2013 ICCP Carbon Materials WG exercises.

Fig. 16. Comparative analyses of the average values of the level of overall agreement performed by each analyst in the exercises 2009-2013.

Table 1. Classification system for textural components (according to ASTM, 2013)

Textural type	Description
Isotropic phase	Binder phase carbon texture that exhibits optical properties that are the same in all directions when viewed with an optical microscope having polarized light, and crossed nicols
Binder phase	Continuous solid carbon matrix formed during the thermoplastic deformation of coal macerals that become plastic during carbonization
Anisotropic	Exhibiting optical properties of different values when viewed with an optical microscope having polarized light, and crossed nicols
Punctiform (incipient anisotropic phase)	Binder phase carbon texture having a domain size (less than $0.5\mu\text{m}$) that is near the resolution of the light microscope
Mosaic	Circular anisotropic phase, subdivided into fine ($\sim 1\mu\text{m}$), medium ($1-5\mu\text{m}$), coarse ($5-10\mu\text{m}$) size categories
Fiber	Flow type, needle anisotropic phase subdivided into fine ($\sim 5\mu\text{m}$), medium ($5-10\mu\text{m}$), coarse ($10-20\mu\text{m}$) size categories
Ribbon anisotropic phase	Group of binder phase anisotropic carbon textures distinguished by their ribbon -like domains [that is length (L) to width (W) ratio of $L > 4W$];
Domain	Region of anisotropy in a carbon form that is distinctively marked by its isochromatic boundary and cleavage

Table 2. Samples type and selected procedures to obtain the samples

Sampling phase/ no. exercise	Type of samples
1	Calcinated petroleum coke (Brazi and Conoco), coal-tar pitch coke, calcinated anthracite.
2	Coal-tar pitches, type A (binder pitch) and type C (impregnating pitch). Samples were pyrogenated in an electric oven at 480, 500, 800 and 1000 °C, with a heating rate of 2-2.5 °C/min and a soak time of 1-2 hours. Temperatures of 480-500 °C were used to reach the mesophase formation and evolution, and that of 800 °C (in case of type C pitch) and 1000 °C (in case of type A pitch) to get the re-backing stage after impregnation and respectively, the backing phase corresponding to the industrial processes.
3	Steel electrodes (diameter of 400 mm): baked, re-baked and graphitized samples.
4	Anodes (diameter of Ø 50 mm). Cathode blocks having a non-regular size.

Table 3. Characteristics of calcinated petroleum cokes and calcinated anthracite

Characteristic	Petroleum coke		Anthracite
	Brazi	Conoco	
Moisture (%)	0.50	0.05	4.00
Volatile matter (% , db)	0.30	0.30	2.00
Ash (% , db)	0.70	0.13	2.00
Fixed carbon (%)	99.00	99.57	96.00
Total sulphur (% , db)	2.80	0.56	0.50
Real density (g/cm ³)	2.03	2.12	-

Corrected: were included all the values to the second decimal point

Table 4. Characteristics of coal-tar pitches

Characteristic	Pitch type	
	A Binding (VFT Rutgers)	C Impregnation (Deza-Cech)
Softening point (Mettler, °C)	109.4	85.8
CCR ¹⁾ (coke value) (%)	55.4	45.2
Moisture (%)	0.1	1.8
Ash (% , db)	0.15	0.09
Total sulphur (% , db)	0.61	0.60
TI ²⁾ (%)	29.9	15.2
QI ³⁾ (%)	7.6	2.0

¹⁾ Alcan coking index

²⁾ Toulene insoluble

³⁾ Quinoline insoluble

Table 5. Classification scheme of optical appearance proposed to participants

Origin	Optical type	Optical texture	Size	Porosity	Inclusions
Pet coke	Isotropy	Mosaic	Punctiform	Voids	Insolubles
Binder pitch coke	Anisotropy	Fiber/ Flow type	Fine	Cracks	Mineral Matter
Impregnating pitch coke		Ribbon	Medium		
Anthracite		Domain	Coarse		

Table 6. Evaluation of results for solid carbon precursors analyzed in 2009 and 2010

Petrographic textures		2009				2010				
		Petroleum coke	Binder pitch	Impregnated pitch	Calcinated anthracite	Average 2009	Binder pitch	Impregnated pitch	Average 2010	
Type	Isotropic	92.0	84.0	95.0	64.0	83.8	90.0	91.0	90.5	
	Anisotropic	83.0	74.0	82.0	61.0	75.0	78.0	78.0	78.0	
Shape	Punctiform	99.0	90.0	98.0	100.0	96.8	95.0	98.0	96.5	
	Mosaic	Fine	98.0	93.0	98.0	98.0	92.5	90.0	92.0	91.0
		Medium	93.0	79.0	98.0	100.0	90.8	90.0	87.0	88.5
	Coarse	92.0	80.0	95.0	96.0	90.8	90	87.0	88.5	
	Average	94.3	84.0	97.0	98.0	96.8	95.0	92.0	93.5	
	Fiber	Fine	84.0	100.0	99.0	100.0	95.8	89.0	100.0	94.5
		Medium	79.0	100.0	98.0	100.0	94.3	92.0	98.0	95.0
Coarse		91.0	100.0	96.0	100.0	96.8	97.0	94.0	95.5	
Average	84.7	100.0	97.7	100.0	95.6	92.7	97.3	95.0		
Ribbon	90.0	100.0	82.0	100.0	93.0	95.0	93.0	94.0		
Domain	85.0	95.0	76.0	95.0	87.8	92.0	81.0	86.5		
Average value		89.7	89.6	89.7	88.3	89.3	90.6	89.8	90.2	

Table 7. Evaluation of results for carbon products analyzed in 2011 and 2013

Petrographic textures		2011			2013				
		Backed	Re-backed	Graphitized	Average 2011	Anode	Cathode blocks	Average 2013	
Type	Isotropic	97.8	95.8	86.0	93.2	96.0	73.0	84.5	
	Anisotropic	87.3	90.0	81.0	86.1	94.0	75.0	84.5	
Shape	Punctiform	99.8	100.0	99.0	99.6	100.0	100.0	100.0	
	Mosaic								
		Fine	97.4	100.0	88.0	95.1	97.0	99.0	98.0
		Medium	87.2	95.3	78.0	86.8	86.0	97.0	91.5
		Coarse	85.0	93.7	74.0	84.2	73.0	97.0	85.0
		Average	89.9	96.3	80.0	88.7	85.3	97.7	91.5
	Fiber								
		Fine	94.9	87.0	97.0	93.0	93.0	98.0	95.5
		Medium	86.0	80.8	86.0	84.3	82.0	93.0	87.5
		Coarse	88.0	84.8	95.0	89.3	78.0	86.0	82.0
		Average	89.6	84.2	92.7	88.9	84.3	92.3	88.3
	Ribbon		89.9	90.1	97.0	92.3	83.0	84.0	83.5
	Domain		88.8	94.3	79.0	87.4	82.0	81.0	81.5
Average value			91.9	93.0	87.8	90.9	89.2	86.1	87.7

Highlights

- We report a method for the evaluation of petrographic textures representing the structural organization of the organic matter derived from coal and petroleum and their interaction phenomena in the making of steel electrodes, anodes and cathode blocks.
- We demonstrate the utilization of existing ASTM classification system applied for textural components in metallurgical coke, to carbon materials textural characterization.
- We assess the results based on the "*raw agreement indices*" statistical method which counting not only the analysts' opinion correct answers, but all of the knowledge and experience of the participants.
- We prove a great homogeneity in the results, the mean value being 90.36%, with the minimum value of 83% and maximum value of 95%.

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- Classification of metallurgical coke optical texture is used for carbon materials
- Results were based on the "*raw agreement indices*" statistical method
- Results prove participants answers great homogeneity with a mean value of 90.36%