Fuel 117 (2014) 598–607

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Coke–pitch interactions during anode preparation

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HIGHLIGHTS

- Study of coke pitch interaction by XPS, FTIR and sessile-drop techniques.
- Interactions of three cokes and two pitches were studied.
- Studied calcined coke and coke–pitch by FTIR–DRIFT, not reported in published article.
- Atomic wt% and functional groups present on coke and pitch surfaces analyzed by XPS.
- Wetting was correlated with the functional groups and evidence of reaction found.

ARTICLE INFO

Article history:
Received 4 July 2013
Received in revised form 19 August 2013
Accepted 6 September 2013
Available online 21 September 2013

Keywords:
Petroleum coke
Coal tar pitch
Wettability
Contact angle
Coke–pitch interactions

ABSTRACT

The information on the interactions between coke and pitch is of great value for the aluminum industry. This information can help choose the suitable coke and pitch pairs as well as the appropriate mixing parameters to be used during the production of anodes. In this study, the interaction mechanisms of pitch and coke at the mixing stage were studied by a sessile-drop test using two coal-tar pitches as the liquid and three petroleum cokes as the substrate. The results showed that the coke–pitch interactions are related to both pitch and coke chemical compositions. The contact angle of different coke–pitch systems decreased with increasing time and temperature. At high temperatures, decreasing the pitch viscosity facilitated the spreading of pitch and its penetration into the coke bed. The chemical behavior of petroleum cokes and coal tar pitches were studied using the FT-IR spectroscopy and XPS. The results showed that the wettability behavior of cokes by pitches depends on their physical properties as well as the presence of surface functional groups of coke and pitch which can form chemical bonds.

1. Introduction

Coal tar pitch is widely used as a binder for the granular material (also called the filler) during the carbon anode production in aluminum industry because of their excellent binding properties. In general, the preparation of carbon anodes involve the following three steps: mixing calcined petroleum coke with recycled anodes and butts (all of which constitute the granular material) with the binder pitch to make an anode paste, vibro-compacting or pressing this paste to form green anodes, and finally baking the green anodes to produce baked anodes that are consumed during the alumina electrolysis for aluminum production.

The final properties of baked carbon anodes are partly determined by the interactions that take place in the kneader during the mixing of the paste [1–3]. Pitch has to penetrate through coke pores and fill the voids between the coke particles. Good interaction between coke and pitch is an essential condition for the generation of satisfactory bonding between these two components. The wettability of coke by pitch is a direct indication of the degree of their interaction. The interaction between the filler and the binder depends on the characteristics of the binder (softening point, chemical composition, surface tension, viscosity) and the coke (particle size, texture, chemical functional groups at the surface, porosity, etc.) [4]. A number of authors found that coal tar pitches behave as Newtonian fluids within the temperature range of 140–231 °C at a shear rate ranging from 0.13 to 7 s^{-1} [5–7]. It implies that pitch viscosity does not vary with the shear rate at constant temperature and pressure during mixing in the kneader. However the mixing efficiency of the kneader is important because it helps disperse and spread pitch around the aggregate and improves the contact [7].

During anode baking, the carbonization of pitch takes place. New bonds form between the granular material and the carbonized pitch. This keeps the structure intact [8]. Wetting and,

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0016-2361/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2013.09.015

consequently, the quality of interactions between these two components greatly affect the final anode properties. The aim is to produce high density, low electrical resistivity, and structurally sound anodes with good mechanical properties. Therefore, choosing a coke–pitch pair that has a tendency to form bonds is the first important step for reaching this goal.

The wettability of calcined coke by a molten pitch drop can be characterized with the contact angle formed between the molten pitch drop and the coke bed. The first widely accepted correlation between the interfacial tension and the contact angle for a liquid drop on a solid surface is expressed by the following equation suggested by Young in 1805 [9]:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta \quad (1)$$

where γ_{sv} is the interfacial tension of the solid–vapor interface, γ_{sl} is the interfacial tension of the solid–liquid interface, γ_{lv} is the interfacial tension of the liquid–vapor interface, and θ is the contact angle. γ_{lv} is also known as the surface tension.

The calcined petroleum coke is one of the raw materials used for anode production. Various authors studied the chemical structure of green petroleum cokes by different analytical methods such as FT-IR and XPS for different applications. The importance of calcined coke is not just limited to anode production. It is important to know the chemical structure and the sulfur content of petroleum coke as they are used as fuel in boilers to produce electricity and are attractive feedstock for gasification. Petroleum coke is also utilized in coal blends that are commonly used in steel plants. The chemical functionality often has an effect on petroleum coke [10].

No significant literature is found on the utilization of FT-IR on calcined coke as the calcined coke has lower absorption characteristics with respect to baseline levels [10]. The presence of aromatic hydrocarbons in petroleum cokes may be responsible for the chemical activity during the coking process. Different authors studied the XPS spectra of green petroleum coke and carbonaceous materials and found that they contain mostly carbon. In addition, they contain oxygen, nitrogen, sulfur, calcium, and sodium [11–14].

A qualitative analysis of different functional groups present in calcined coke was carried out by FT-IR analysis; and based on this information; a quantitative analysis of these functional groups has been done by XPS analysis. XPS is one of the conventional methods better suited to perform quantitative analyses. To understand the nature of interaction between calcined petroleum coke and coal tar pitch, it is also important to study the chemical structure of pitch. The purpose of this study is to evaluate the degree of wetting of cokes by pitches and to investigate their interactive characteristics.

2. Materials and methodology

2.1. Materials

In this study, commercially available calcined petroleum cokes and coal tar pitches have been used for all the tests. The physical and chemical properties of the cokes and the pitches are given in Tables 1 and 2.

2.2. Sessile drop experimental system

The sessile-drop experimental system consists of a tube furnace (thermolyne 21100), an inconel tube with a pitch injection system, a graphite sample crucible, a digital video camera (B/W, APPRO, model KC), and a secondary rotary vacuum pump (GE, Precision Vacuum Pump, Model D25) (see Fig. 1). The compacted coke powder is placed in the sample crucible. The injection chamber holds the solid pitch sample. This chamber has a small hole at the bottom and is placed just above the coke sample during the experiment.

Table 1
Physical and chemical properties of cokes used in the study.

Properties	Calcined petroleum coke		
	Coke 1	Coke 2	Coke 3
Bulk density[a] (kg/m^3)	870	820	920
Sp. electrical resistivity (ohm m)	0.00099	0.00107	0.00094
CO_2 reactivity (%)	14.5	6.8	3.9
Air reactivity (% per min)	0.23	0.14	0.1
Porosity for coarse particle[b] (%)	21.5	18.1	13.7
Porosity for 125 μm particle[b] (%)	6.2	5.85	5.13
Crystalline length (Å)	28.5	29.7	28.2
Ash content[c] (%)	0.2	0.2	0.13
Moisture content (%)	0.1	0.04	0.05
C (wt%)	95.37	95.34	95.34
N (wt%)	0.99	0.91	0.89
H (wt%)	0.17	0.16	0.15
S (wt%)	1.91	2.41	2.57

[a] Measured by ASTM D4292-10.
[b] Measured by ISO 1014:1985.
[c] Measured by dry basis.

Table 2
Physical and chemical properties of pitches used in the study.

Properties	Coal-tar pitch	
	Pitch 1	Pitch 2
Ash at 900 °C (%m/m)	0.12	0.14
β Resin (%m/m)	22.3	23.2
Density at 20 °C (g/ml)	1.320	1.320
Quinoline insoluble (%m/m)	8.5	5.7
Toluene insoluble (%m/m)	30.8	28.9
Coking value (%m/m)	60.4	57.7
Softening point (°C)	118.2	120.5
Dynamic viscosity 170 °C (MPa s)	1710	1210

In this study, two types of coal tar pitch and three types of petroleum coke used by the industry were tested. Coke particles were grounded, and an average particle size of 125 μm was used for wetting tests. This particle size was also used by other researchers [8,15]. The particles were compacted in the sample crucible in order to have a smooth coke bed surface. The experiments were conducted under nitrogen (N_2) atmosphere. There are two entry lines for nitrogen. The main line is directly connected to the Inconel tube for maintaining the inert atmosphere inside this tube. The other line that connects the injection chamber to the inert gas supply carries the N_2 gas necessary for slightly pressurizing this chamber in order to force the liquid pitch out on to the solid sample. Pitch is placed in the graphite injection chamber above the substrate holder. The molten pitch droplet is directly dropped onto the coke substrate by arranging the position of the injection chamber hole. The drop size can be changed by adjusting the hole size. The substrate holder can be removed from the hot region of the furnace by using a specially designed mechanism, and the sample can be quenched for further analysis. A video of the drop is captured for 25 min. The system can capture both static and dynamic images. To measure the contact angle, the FTA 32 software is used. In order to decrease the O_2 and humidity content of N_2, the gas is passed through O_2 (Chromatographic Specialties, Oxygen Trap C36084) and humidity traps (Chromatographic Specialties, Glass Moisture Trap – C36150) before it enters the system. The sessile drop experiments were carried out at two different temperatures (170 °C and 190 °C). For each experiment, the contact angle was taken as the average of the angles measured on two sides of the drop. Each experiment was repeated twice. Three different cokes and two different pitches were studied using a sessile-drop system in order to understand their interactions. A comprehensive understanding of these interactions helps produce better quality carbon anodes for use in primary aluminum production.