Microstructural Representation and Transformation of Petroleum Coke via Self-Developed HRTEM Analytic Technique

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Abstract

Carbon electrodes for aluminium electrolysis are mainly made of petroleum coke (PC, accounting for 85 wt.%). The amorphous phase of PC poses a challenge for the precise microstructure analysis, thus hindering the development of carbon electrode preparation processes. In recent work, we developed an intelligent lattice fringe extraction technique for amorphous carbon materials based on high-resolution transmission electron micrographs (HRTEM) detection and image binarization. The microstructural arrangement state and data (lattice length, orientation, curvature, stacking, etc.) of green petroleum coke (GPC) and calcined petroleum coke (CPC) were obtained via this integrated HRTEM analytic technique. Then the atomistic representations of GPC and CPC incorporating actual parameters were constructed for comprehensive observation and simulation via an automated modelling strategy. Furthermore, the microstructural transformation pattern of GPC across the industrial calcination temperature range (25 to 1600 °C) was explored and quantified based on a series of microstructural data at discrete temperature stages.

Keywords: Petroleum Coke, HRTEM, Lattice Fringe, Microstructural Analysis, Atomistic Modeling.

1. Introduction

Petroleum coke (PC) is the primary raw material for carbon electrodes in aluminum electrolysis cells, accounting for over 85 wt.% of the electrode composition [1]. PC is categorized as an amorphous carbon material with a complex microstructure characterized by the intertwining of sp2 and sp3 hybridized carbon atoms, diverse ONS functional group configurations, and the presence of hydrogen bonds [2]. Previous research has yet to provide an in-depth exploration of such intricate microstructural characteristics.

During the preparation of carbon electrodes, green petroleum coke (GPC) undergoes a calcination process to form calcined petroleum coke (CPC). This process involves pyrolysis, polymerization, and reordering of the carbon structure [2]. However, the precise mechanisms governing the microstructural evolution during calcination remain largely unexplored, representing a significant research gap. Consequently, in industrial production, extensive manual adjustments of equipment parameters are often required to accommodate the variations in GPC properties. It poses a bottleneck to the intelligent manufacturing of metallurgical carbon materials and the broader aluminum electrolysis sector. Addressing this bottleneck necessitates not only the precise characterization of PC microstructural features at the atomic scale but also a comprehensive understanding of the structural evolution across multiple calcination temperature stages.

Recent advances in the analysis of carbon network chains (aromatic layers) in amorphous carbon materials such as coal have provided new insights into the structural characteristics of such systems. Mathews et al. [3–5] employed the Materials Studio software platform in conjunction with high-resolution transmission electron microscopy (HRTEM) and Perl scripts such as Fring3D and Vol3D to achieve automated modeling of coal, coke, and carbon black. Louw et al. [6, 7] developed the Stack software based on Matlab, enabling quantitative analysis of aromatic layer stacking configurations by controlling center-to-center distance, nearest neighbor distance, and angular orientation. This approach allows the extraction of secondary, tertiary, quaternary, and quinary stacking configurations, facilitating subsequent data processing and calculation. Furthermore, Changan Wang et al. [8] investigated the curvature properties of aromatic layers in amorphous carbon materials using the Curvature script based on Matlab, segmenting the lattice fringes based on length and angular parameters to analyze directional layer curvature. Simultaneously, Huang Yang [9] et al. developed Perl scripts such as Cross_link.pl to connect aromatic layers and optimize the structural configuration of curved aromatic layers in activated carbon.

In this study, we integrated these advanced HRTEM-based methodologies to develop a comprehensive and intelligent lattice fringe extraction technique for carbon materials, allowing for a detailed characterization of the microstructural features of both PC and CPC. Additionally, we designed a customized Packmol script [10] to construct a multi-scale and visualizable model that effectively captures the microstructural characteristics and composition of PC and CPC. Furthermore, we investigated the evolution of PC microstructures, including lattice fringe length, stacking, orientation, and curvature, across various calcination temperature stages. The proposed intelligent lattice fringe extraction technique and the associated findings provide a solid theoretical foundation for the intelligent manufacturing of metallurgical carbon materials.

2. Methods

2.1 Coke Sample

The components of GPC samples used in this work are shown in Table 1, Cokes 1, 2 and 3 being respectively produced in Shandong Province, in Zhejiang Province, and at Tianjin Municipality, China. The samples were ground and sieved, with the −106 μm fraction selected for calcination. Approximately 70 g of dried powder was weighed for each batch and placed into a graphite crucible, which was then positioned at the center bottom of an alumina crucible. The remaining space in the alumina crucible was filled with landfill material to provide an oxygen-isolated environment during calcination. The samples were held at a setting temperature for 4 h to complete the calcination process. The setting temperature is in the range from 298 to 1873 K. The heating rate was set at 5 K/min below 1273 K and 3 K/min above 1273 K. The furnace model used was KSL-1700X, manufactured by Hefei Kejing Materials Technology Co., Ltd.

Table 1. Ultimate analyses of green petroleum coke samples (wt.%).

Samples	C	H	N	S	O
Coke 1	89.53	3.38	1.27	2.45	2.27
Coke 2	89.08	3.55	1.37	2.67	3.33
Coke 3	86.47	3.46	1.77	4.19	4.11

4. Conclusions

This work presents an HRTEM analytic technique for the intelligent extraction and analysis of lattice fringes in carbon materials, developed through the integration of HRTEM imaging, binary image processing techniques, and customized Matlab and Perl scripts. The developed technique enables quantitative analysis of lattice fringe characteristics such as length, stacking, orientation, and curvature. It fills a critical gap in the precise structural analysis of aluminum electrolysis carbon materials and applies to a broad range of studies on the microstructural evolution of various carbon-based materials.

Representative models of PC were constructed at the molecular scale, 3D microcrystalline scale, and 3D nanoscale. The DFT calculations were used to generate FT-IR and XRD spectra, which confirm the aromaticity and degree of ordering in the constructed models. For the three coke materials tested, the multi-level validation affirms the accuracy and reliability of the models. Beyond visualizing the microstructure of calcined coke, these models also provide a robust platform for quantitative simulations and molecular dynamics studies of various reactive processes in metallurgical carbon materials.

The HRTEM analytical technique, in combination with mathematical fitting, was employed to continuously and quantitatively evaluate the evolution of PC microstructures as a function of calcination temperature. In the temperature range of 873–1873 K, the microstructural parameters exhibit excellent agreement with Logistic regression models. Below 873 K, the structure undergoes slight disordering, while above this threshold, a significant increase in structural ordering is observed. Mathematical equations derived from the fitted curves enabled the reliable prediction of key microstructural features of the three tested coke samples at any given temperature.

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6. References

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