



Structural evolution during the catalytic graphitization of a thermosetting refractory binder and oxidation resistance of the derived carbons

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HIGHLIGHTS

- Structural evolution during pyrolysis of novolac resin containing H₃BO₃ or B₂O₃.
- The catalytic graphitization depends on B–O–C formation and cleavage.
- Composition, bond strength and crystallization controlled the carbons' reactivity.
- Better oxidation resistance can be attained without the carbon's crystallization.

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ABSTRACT

Carbon-containing refractories' (CCRs) thermomechanical properties depend on the presence of carbonaceous phase with a structure and features similar to those of graphite. Based on this, boron oxide and boric acid were used to induce graphite generation during the pyrolysis of novolac resin (binder for CCRs) to provide an additional source of crystalline carbons. In this study, the structural evolution leading to crystallization of the derived carbons was studied via Fourier Transform Infrared (FTIR) spectroscopy. The results showed that the carbons graphitization was as a result of the formation and cleavage of the B–O–C bond during heat treatment. The lower binding energy of this bond compared to plain C–C bond permits carbon atoms rotation and restructuring necessary for graphite generation during the pyrolysis operation. Furthermore, the research investigated the oxidation resistance of the derived carbon samples with the aid of thermogravimetric (TGA) and differential scanning calorimetry (DSC) equipment. The influence of different mixing routes at the preparation stage and hexamethylenetetramine (HMTA) addition to the resin formulations on the carbons' oxidation resistance was also examined. The analysis provides insight on the parameters that control the oxidizing behavior of the different samples obtained based on these variations. Several factors including graphitization, composition and atoms bond strength were observed to influence their performance when the carbons were exposed to the non-reducing environment at high temperatures up to 1000 °C.

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1. Introduction

Carbon-containing refractories' (CCRs) thermomechanical performances are significantly influenced by the added graphite and binder component [1,2]. The carbonaceous phase acts as a non-wetting material, which minimizes slag penetration into the brick

during steel-making applications [3]. The polymer products used to link the coarse and fine refractory particles together provides green mechanical strength, reduce porosity, and acts as an additional carbon source.

Due to environmental concerns, thermosetting resins (novolac, resole) have replaced the conventional binders such as coal tar or pitch, which produces graphitizable carbon with superior oxidation resistance. Phenolic resins emit minimal polycyclic aromatic hydrocarbons and other toxic substances during their pyrolysis and therefore provide greater health benefits [4,5]. Unlike pitch-bonded

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bricks, which show expansion after tempering, resin-bonded ones exhibit lesser shrinkage irrespective of the carbon content and their usage (thermosetting resins) offers the advantage of cold-mixing [2]. Nevertheless, the significance of carbon derived from these resins is still limited because they possess poor oxidation resistance (because of their isotropic nature) and cannot compensate for excess stresses (except by microcracks formation) due to their hardness and brittleness [1]. These types of organic precursors do not undergo reconstructive transformation during heating in an inert environment because their pyrolysis is exclusively a solid state reaction, which occurs without the formation of liquid or semi-liquid components.

Carbons' oxidation resistance depends on their accessibility by the reacting media and bond strength between their atoms. Their composition and atomic arrangement also influence this property. Crystalline carbons have improved oxidation resistance than the amorphous or glassy ones [6] due to the reduced amount of edge site atoms and their anisotropic nature [7–9]. Therefore, graphite's generation during pyrolysis of non-graphitizable organic precursors such as thermosetting resins should reduce the resulting carbons' reactivity in oxygen.

Moreover, the depletion rate of carbon in CCRs will determine their service life and performance consistency in terms of thermal shock resistance and infiltration. Consequently, there is an increasing interest to achieve the graphitization of phenolic resin carbons using processing parameters that can be adopted for the production of CCRs. The use of certain additives has been reported to induce crystallization of phenolic resin carbons through a process referred to as catalytic graphitization [10–12]. The results obtained from such studies confirmed an improvement in the oxidation resistance of the derived carbons [13,14]. In additions to this benefit, the CCRs developed based on in-situ graphitization of the thermosetting resin component have improved mechanical properties [1,15].

The catalytic graphitization of novolac resin containing either boric acid or boron oxide was reported by Talabi et al. [16]. The research focused on the role that some processing parameters such as mixing technique, heat treatment procedure and heating rate have on the amount of generated crystalline carbons. However, the reaction that led to graphite generation during the modified-resin carbonization was not analyzed. Consequently, this study investigates and discusses the structural evolution that occurs during the thermal treatment of the H_3BO_3 and B_2O_3 -modified novolac resin and provided insight on the mechanism leading to their graphitization. Furthermore, the oxidation stability of the resulting carbon was studied with the aid of thermogravimetric (TGA) and differential scanning calorimetry (DSC) equipment. The carbons reactivity in an oxidizing environment and the attained graphitization level were compared to ascertain the relationship between both parameters.

2. Experimental procedures

Novolac resin (Nv) was selected for investigation as an additional source of crystalline carbons in carbon-containing refractories. Firstly, a reference sample was prepared from a mixture of novolac resin and 10 wt% hexamethylenetetramine (HMTA, $d < 200 \mu\text{m}$). Thereafter, commercial novolac resin (Nv) was mixed with either 6 wt% boron oxide or 10 wt% boric acid (the graphitizing agents). The weight percentages of H_3BO_3 and B_2O_3 in the formulation are equivalent. Also, the effect of HMTA incorporation into the modified resin was investigated. The formulations' components were mixed primarily with the aid of a mechanical mixer at 30 rpm

for 20 min for homogeneous dispersion of the additives within the resin. The effect of additional ultrasonic mixing (for 15 min) or vacuum degassing (for 10 min) during the preparation stage on oxidation resistance of the derived carbons were also studied. These procedures were incorporated to facilitate proper dispersion of the additives and remove oxygen introduced during mechanical mixing respectively. Each of the prepared compositions was poured into an alumina crucible, covered with disk and embedded in a refractory box filled with coke to create a reducing environment during the step-wise pyrolysis procedure. The process involved heating the samples to 100°C with a hold time of 4 h before raising the temperature to 500°C with a hold time of 1 h and then to 1000°C and keeping it at that temperature for 5 h. The heating rate of $3^\circ\text{C}/\text{min}$ was employed for the entire heating steps. The raw materials information with samples and preparation designations, were presented in Table 1. The B and H represent B_2O_3 and H_3BO_3 respectively. The number by the side of the different additives stands for their percentage weight in the formulation (e.g., 6B stands for 6 wt% B_2O_3). The letter "M" in the sample designation stands for "mechanical mixing," the "U" represents "additional ultrasonic mixing" and "V" stands for "additional vacuum degassing."

After carbonization, the samples were cooled to room temperature inside the muffle furnace at a cooling rate of $\sim 16^\circ\text{C}/\text{min}$ and ground in an AMEF vibratory disc mill for 12s. A NETZSCH STA 449F3 (Netzsch Inc., Germany)-type thermogravimetric (TGA) and differential scanning calorimetry (DSC) analyzer was used to determine the samples' behavior in an oxidizing environment. The apparatus detects mass loss and heat flow with a resolution of 0.001 g and 0.00001 mW/mg respectively, as a function of temperature and time. Before carrying out the test, the samples were evenly distributed in an alumina sample pan. The analysis was performed in synthetic air (80% N_2 , 20% O_2) at $50 \text{ cm}^3/\text{min}$ flow rate starting from 30°C to $1000^\circ\text{C} \pm 10^\circ\text{C}$ with $10^\circ\text{C}/\text{min}$ heating rate. Due to the presence of impurities, the thermogravimetric (TG) curves were normalized to eliminate the contribution of the non-carbon material. Firstly, the inflection point temperature, which represents the onset of carbons oxidation was determined from the non-isothermal TG curves as depicted in Fig. 1. The final residual mass (RM_f) was then subtracted from the one at the onset of carbon oxidation (MO_i) to obtain the actual carbon loss (x). Subsequently, the actual residual mass of carbons at the end of the measurement (RM_a) was calculated according to equation 1.

$$RM_a = 100 - (MO_i - RM_f) \quad (1)$$

RM_a was used to describe the overall oxidation resistance of the polymeric carbons. Moreover, the information from the DSC curves was used to complement the deductions from the TG curves and FTIR spectra.

Fourier Transform Infrared (FTIR) spectroscopy was used to study the structural evolution that occurs during thermal cross-linking ($100^\circ\text{C}/4\text{h} + 230^\circ\text{C}/1\text{h}$), carbonization ($100^\circ\text{C}/4\text{h} + 230^\circ\text{C}/1\text{h} + 500^\circ\text{C}/1\text{h}$) and graphitization ($100^\circ\text{C}/4\text{h} + 230^\circ\text{C}/1\text{h} + 500^\circ\text{C}/1\text{h} + 1000^\circ\text{C}/5\text{h}$) stages. The FTIR spectra were recorded via a Varian 640-IR spectrometer between 400 and 4000 cm^{-1} , 64 accumulations, and 4 cm^{-1} resolution using the standard KBr method. For this analysis, each sample and KBr powder were dried in an oven at 110°C for 24 h to remove moisture. 200 mg of fine KBr was mixed with 2 mg of the carbon samples, pulverized and then pressed to form transparent pellets that were used for the characterization.

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