Effect of Cu/Si Additive on the Microstructure of Pyrolysis Carbon Derived from Phenolic Resin

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Abstract. Phenolic resin has been widely applied as a carbonaceous binder in the field of carbon composites and carbon materials. The microstructure of pyrolysis carbon that derived from carbonaceous binders played an important role in the properties of carbon-containing refractories. In this study, the effects of copper and silicon on the pyrolysis behavior of phenolic resin and the microstructure of the pyrolysis carbon were investigated by using thermosetting phenolic resin as raw material, and using silicon powder (99%, 200 mesh) as well as copper nitrate (AR, w(Cu(NO₃)₂) ≥ 99%) as additives. The results showed that the copper nano-particles in-situ formed from copper nitrate could be served as catalyst in the pyrolysis process of resin. Catalytic synthesis of carbon nanofibers could improve the degree of carbonization with pyrolysis carbon microstructure at low temperature (below 800 °C). The carbon nanofibers had lamellar structure and layered stacking characteristic. Silicon carbide whiskers were produced by Cu-doping phenolic resin with copper and silicon at 1400 °C.

1. Introduction
Phenolic resin has been widely applied as binding agent for Carbon composites, especially used as carbonaceous binder in refractories [1–3]. Its outstanding viscosity is given by the unique molecular structure. It can be easily moistened, dispersed and shaped. At the same time, the pyrolysis-curing property of phenolic resin provides carbon bond in the formation of three-dimensional network structure improving the mechanical strength of the brick. However, some unfavorable behavior and performance are recognized when phenolic resin was carbonized. The isotropic glassy carbon structure derived from phenolic resin is difficult to be graphitized even at high temperature, resulting in brittleness and poor oxidation resistance [4–6]. The microstructure of carbon derived from carbonaceous binders could affect properties of carbon-containing refractories greatly. Researchers pay more attention to modify phenolic resin by in-situ formation of carbon nanofibers (CNFs) or carbon nanotubes (CNTs) and other low-dimensional carbon nanostructures in the phenolic resin-derived carbon, whose graphitization degree and oxidation resistance are improved [7, 8]. At the same time, ceramic phase are formed in situ with the matrix components in the carbon-containing refractories to improve the high-temperature strength and toughness [9–11].

Recently, different researches induce the crystallization of non-graphitic phenolic resin binders, so-called catalytic graphitization. During pyrolysis of phenolic resin, glassy isotropic carbon converts into graphitic carbon through addition of catalytic agents. Transition metallic elements, Ni, Cu, Fe and compounds are used to modify phenolic resin. Stamatin et al. used Ferrocene to modify phenolic resin and synthesizing a large number of multi-walled carbon nanotubes (MWCNTs) in the pyrolytic carbon structure after heat treatment at 900 °C in Argon atmosphere [12]. Hu et al. reported a novel and
simple approach for preparing graphitic carbon nano fibres through the in-situ catalytic graphitisation of phenolic resin using NiC$_2$O$_2$·2H$_2$O nanofibres as both catalyst precursors and templates. Graphitisation begins at 1073 K with the aid of nickel as the graphitisation catalyst and Carbon nanofibres fabricated at 1273 K have highly well-defined C (002) lattice fringes [13]. Wang et al. used Co-Ni bimetallic catalyst investigating the catalytic graphitization of phenolic resin at different temperature under Ar atmosphere. The results show the optimum catalytic graphitization temperature of phenolic resin is 800 °C, and both carbon nanotubes and carbon onions are formed in the final products [14]. Most researches are related with catalytic graphitization of phenolic resins. The central concept behind this approach lies in in-situ catalytic carbon matrix graphitization, such as carbon nanofibers or carbon nanotubes, which are catalytically deposited by pyrolysis gases to produce secondary carbons with high degree of graphitization. However, the temperature of synthesis CNFs or CNTs by transition metal catalysts is higher. And phenolic resin will volatilize many small molecules, such as CO and H$_2$ when the temperature of pyrolysis is 500-800 °C. It is significant to reduce the temperature of catalytic synthesis CNFs, CNTs or carbon nanostructure by metal catalysts. More carbon derived from phenolic resin can be obtained.

Besides, silicon carbide (SiC) has received extensive attention because of its good slag resistance, high hardness, excellent corrosion resistance, high thermal stability and resistance to wetting from metallic or alkaline slags [15–17]. Silicon carbide could be formed easily in the central position of carbon-containing refractory used liquid phenolic resin as carbon source, improving the high temperature strength and melt erosion resistance of the material. Such as Deng et al. reported that Sintering temperatures of 1200 °C could generate SiC phases in Al$_2$O$_3$-C refractory samples. SiC whiskers were formed at different sintering temperatures. The cold crushing strength and cold modulus of rupture of Al$_2$O$_3$-C refractory samples increased to 148.67MPa and 33.02 MPa, respectively [18]. Shantanu K et al. found SiC phase even at temperatures lower than the melting point of Si in Al$_2$O$_3$-C slide gate plate refractories. And the improved oxidation resistance and high temperature mechanical properties were ascribed to the SiC whiskers [19]. Zhang et al. found that at 1200 °C, addition of Si led to formation of SiC, Si$_3$N$_4$ and SiO$_2$ [20]. Zhang et al. prepared ultra-long SiC/SiO$_2$ core-shell nanowires on a graphite felt coated with Ni(NO$_3$)$_2$ via a conventional molten-salt-mediated carbothermal reduction route at 1400 °C, using silica fume and phenolic resin as starting materials. As-synthesized nanowires were 150-500 nm in diameter and up to several hundred microns in length. Therefore, these results demonstrated that use of catalysts not only effective in the reduction of synthesis temperature of SiC but also beneficial of its morphology control.

Compared with the traditional transition metal catalysts, using Cu metal catalytic can in situ form graphitic carbon nanofibres in the matrix of carbonised phenolic resins. The glassy isotropic carbon of the phenolic resin-pyrolysed carbon can be transformed into graphitic carbon by catalytic graphitisation. In this paper, a metal catalytic Cu was introduced as metal catalyst to synthesize CNFs or CNTs by using liquid thermosetting phenolic resin as carbon source, copper nitrate as catalyst precursor. The effect of catalytic elemental Cu on the pyrolysis of phenolic resin and the micro-structure evolution, graphitization level and oxidation resistance of the modified phenolic resins at different heat treatment temperature are explored. At the same time, the effects of Cu and Si powder on the microstructure of the carbon derived from phenol resin were investigated, and the corresponding reaction mechanisms were discussed based on the experimental results and thermodynamic analysis.

2. Experimental

2.1. Raw materials and sample preparation

Liquid thermosetting phenolic resin (Wuhan Lifa Chemical Co., Ltd., 2221) and Silicon powder (99%, 200 mesh, Guoyao Chem. Co. Ltd., Shanghai China) were used as raw materials. Cu(NO$_3$)$_2$·3H$_2$O (AR, w≥99%) was used as a catalyst precursor, and C$_2$H$_5$OH (BodiChem. Co. Ltd., Tianjin, China) was used as solvent.
Table 1. Compounding of the samples

| Sample | Phenolic resin w/% | Raw materials w/% | Si power |
|--------|-------------------|------------------|---------|
| A      | 100               | 0                | 0       |
| B      | 90                | 0                | 10      |
| C      | 99                | 1                | 0       |
| D      | 89                | 1                | 10      |

The samples are listed in Table 1. According to the plan in table 1, copper nitrate catalyst precursor was dissolved and heated in appropriate amount of alcohol, then it was slowly poured into the phenolic resin raw material and mixture. The silica powder was added to the phenolic resin and the viscosity was adjusted with the help of ethyl alcohol. The copper nitrate catalyst precursor was dissolved in alcohol and added to the resin. Then, silicon powder is added. During all those procedures, every mixture was stirred evenly every time. Pure phenolic resin didn’t undergo any treatment. Mixed solutions of different formulations were obtained, then the solutions were cured at 70 °C for 3 hours, 120 °C for 12 hours and 220 °C for 24 hours, respectively. Finally, cured samples were fired at 5 °C/min in reducing atmosphere (coke bed) until the temperatures is 600, 800, 1000, 1200 and 1400 °C , respectively, holding for 3 hours.

2.2. Characterization

The phases in samples were identified by means of powder X-ray diffraction (XRD) analysis using a Philips X’Pert PRO diffractometer (PANalytical, Netherlands). Spectra were recorded at 40 mA and 40 kV, using CuKa radiation (λ = 0.1542 nm) within the range between 10°and 90° (2θ). The semi-quantitative analysis based on Highscore Plus was carried out to calculate the contents of crystalline phases in samples. Because it is very hard to get a result with enough calculation accuracy using riveted refinement method owing to the existence of little amorphous C in the final products. Microstructures and morphologies of prepared block sample were examined by a field emission scanning electron microscope (FE-SEM, Nova400NanoSEM, Philips, Netherlands, and 15 kV). The samples for SEM were coated with gold and selected area electron diffraction (SAED). Additionally, Thermo gravimetry-differential analysis (TG-DTA, STA449, NETZSCH, Germany) were carried out to investigate the oxidation resistance of the carbon derived from pyrolysis of phenolic resin with a heating rate of 10 °C/min in static air atmosphere. The Raman spectros copy technique (FT-Raman 960 with He-Ne laser, wave-length 633 nm).

Figure 1. XRD patterns of sample A and sample C at different temperatures.
3. Results and discussion

3.1. Raw materials and sample preparation

The XRD patterns of samples A and C prepared at different temperatures were shown in Figure 1.

XRD patterns of sample A indicates that peaks in the 2θ angles is about 25.8° and 43.2° refer to (002) and (100) planes, respectively. With the increase of heat treatment temperature, the bulge near (002) raise gradually. But it is not sharp, meaning that the carbon crystallinity for pure phenolic resin is very limited even heat treated was at high temperature. The glassy isotropic carbon of the phenolic resin-pyrolysed carbon showed non-graphitic features with low toughness and oxidation resistance. The XRD patterns of sample C prepared at temperatures of 600 °C, 800 °C, 1000 °C and 1200 °C are shown. When the copper nitrate catalyst was added into the phenolic resin, due to the decomposition of the catalyst precursor of copper nitrate, the crystalline water in copper Cu(NO3)2·3H2O evaporated as the temperature rises. The precursor of copper nitrate trihydrate catalyst transforms into copper oxide at 170 °C. XRD patterns of sample C indicates that peaks in the 2θ angles is about 43° and 50° refer to Cu diffraction peak was detected. Diffraction peaks of copper oxide (CuO) were not detected, indicating that oxide decomposed by copper nitrate is reduced to metallic copper at temperatures of 600 °C and higher. The reason is that the pyrolysis-curing property of the phenolic resin itself provides CH4, H2 and CO. Copper oxide can be reduced to elemental copper by reducing atmosphere. The formation reactions involved can be summarized as followed:

\[ 4\text{CuO} + \text{CH}_4 \rightarrow 4\text{Cu} + \text{CO}_2 + 2\text{H}_2\text{O} \]  \hspace{1cm} (1)

\[ \text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O} \]  \hspace{1cm} (2)

\[ \text{CuO} + \text{CO} \rightarrow \text{Cu} + \text{CO}_2 \]  \hspace{1cm} (3)

In Equations (1), (2) and (3), at 600°C and higher, the reaction equation \( \Delta G \) is less than 0, indicating that thermodynamics is spontaneous. Graphite crystalline structure is not formed in C specimens and the amount of crystallization of phenolic resin do not increase after pyrolysis under the influence of in-situ nano-Cu formation.

The XRD patterns of B and D samples prepared at different temperatures are shown in Figure 2.

**Figure 2.** XRD patterns of sample B and sample D at different temperatures.

XRD patterns of sample B indicates that when the heat treatment temperature is below 1200 °C, the XRD spectra mainly show the diffraction peaks of silicon and only a small amount of silicon dioxide, meaning that only Si but not SiC was detected. So, the reaction for SiC formation has not started yet. When heat treatment temperature increase to 1400 °C, a small amount of diffraction peaks of SiC appeared at XRD patterns of sample B. However Si still remained as the primary phase, along with
minor SiC, indicating that the reaction occurred but was still far from completion. XRD patterns of sample D is similar to that of sample B at 600 °C. Only Si and a small amount of silicon oxide was detected without any SiC. When the temperature raised to 800 °C, 1000 °C and 1200 °C, Si still remained as the primary phase, along with minor SiO2. But unlike sample B, SiC became the main crystalline phase at 1200 °C. The phase of silicon dioxide was improved, and there was still remaining Si, indicating that the formation reaction of SiC after adding Cu catalyst was promoted and phase pure SiC was obtained. XRD results show that at 1200 °C, only Si was detected, indicating that reaction between Si and C didn’t occur at this temperature. At 1400 °C, Si still remained as the main crystalline phase along with only minor SiC. But when the copper catalyst was added, it was found that SiC increased and Si decreased. The reaction was promoted. Addition of Cu catalyst could promote the synthesis progress of SiC at 1400 °C.

3.2. Raman spectroscopy results

Raman spectroscopy is a molecular spectroscopy technique that has diverse applications in various research fields. Raman spectroscopy is an extremely valuable analytical tool for studying crystalline and amorphous carbon materials. This tool provides good qualitative and quantitative information about various physical properties, such as the amount of crystallization, the amount of order and disorder, and structural defects of carbon materials such as graphite, graphene and etc. Raman spectroscopy of carbon nano-particles reveals distinct peaks in the range of 1000-2000 cm⁻¹, which represents the amount of order and disorder of the carbon structure [22].

![Figure 3. Raman spectra of sample A and sample C at different temperatures.](image)

The D peaks is near 1340 cm⁻¹ in graphite and carbon nanostructures showing the amount of defect and disorder, which means that with the increase of the intensity of D peak, the amount of disorder and defects in the material increased. Corresponding to D peak, the G peaks is at about 1600 cm⁻¹ corresponding to the stretching vibrations of carbon to carbon bonds in the graphite layers. The G peaks show carbon atoms that are spatially coupled in the form of SP² in graphite layers, and, more simply, represent the amount of amorphous carbon graphitization. With the increase of the intensity of G peak, the amount of order and degree of graphitization in the material increased. D-to-G peaks intensity ratio, or G-to-D peaks intensity ratio, in Raman analysis can provide appropriate information of the degree of graphitization, the amount of defects, and the size of the crystallites. Based on this, we can use a parameter which shows the ratio between the intensity of these peaks, which is indicated by the R sign, expressing the intensity ratio of the peak D (I_D) to the intensity of the peak G (I_G) [23]. The larger the R (I_D/I_G) ratio means the less graphitization.

The Raman spectra of sample A and sample C at different temperatures are shown in Figure 3. With the increase of temperature in sample A, the intensity of D peaks increase while the intensity of G peaks decrease. The R ratio increased gradually, which indicated the increase in the percentage of
amorphous carbon from pyrolysis of phenolic resin. The reason is that with the increase of heat treatment temperature, the pyrolysis of phenolic resin produces more gases. Its structure was gradually destroyed, and the defects and vacancy gradually increased. At the same time the isotropic glassy carbon structure derived from phenolic resin was difficult to be graphitized even at high temperature. Therefore, there are more defects. The graphitized structure is difficult to be produced. R value gradually increased, which was determined by the properties of phenolic resin itself. When the intensity of the G peak is much lower than D peak in the phenolic resin, there is a small percentage of the amorphous carbon which is crystalline, limited to the short range order. As a result, the X-ray diffraction pattern of such sample A fully reflects the amorphous results. With increasing temperature in sample C, when the copper nitrate catalyst was added to the phenolic resin, the overall trend of R value also gradually increased. However, under the same heat treatment conditions, the R value of sample C is obviously less than that of sample A, such as when the heat treatment temperature is at 600 °C, the R value of sample C is 0.77, which is obviously less than that of sample C which is 0.89. The results showed that the addition of copper catalyst can catalyse graphitization of phenolic resin matrix to form carbon structure with higher degree of graphitization even at lower temperatures (600–800 °C), which indicates the increase of graphite phase in the amorphous carbon matrix resulting from the pyrolysis of the phenolic resin.

3.3. Microstructural observation by SEM

Microstructures and phase morphologies of as-prepared sample B, sample C and sample D were examined by using FE-SEM. The SEM images of sample C prepared at different temperatures were shown in Figure 4.

![Figure 4. SEM images of sample C at different temperatures: (a), (b) 600 °C, (c) (d) 800 °C.](image)

Figure 4 showed the micrograph images of sample C cured at 600 °C and 800 °C. The SEM images of sample C obtained at 600 °C for 180 min by using Cu catalyst showed that a number of carbon nanofibers were randomly distributed among the metal copper granular particles such as (a). Most of the carbon nanofibers were about 2–5μm in length. The granular particles of Cu were equiaxed with
nano-scale diameters. Some of them were aggregated together to form larger agglomerates, and carbon nanofibers were obtained based on Cu catalyst particles existing in clusters such as (b), (c) and (d) presents typical FE-SEM images of phenolic resin reusing 1.0 wt% Cu catalysts from 3 hours heat treatment at 800 °C. Morphologies of carbon nanofibers in the sample were essentially the same as those in the sample C at 600 °C. Carbon nanofibers and Cu granular particles were also observed. However, with the increase of heat treatment temperature, the number of clusters of carbon nanofibers increased significantly. At the same time, the length of carbon nanofibers increased significantly. Most of the carbon nanofibers were about 5–10 μm in length. The granular particles of Cu were also equiaxed with nano-scale diameters, and the formed agglomerates also got thicker. The SEM results show that the graphite structure is formed in the amorphous carbon matrix resulting from the pyrolysis of the phenolic resin by Cu catalytic. The glassy isotropic carbon of the phenolic resin-pyrolysed carbon can be transformed into graphitic carbon by adding Cu catalytic graphitization and heat treatment temperature. Moreover, it is to be noted that the carbon nanofibers were most probably growth through Dissolution - Precipitation mechanism since spherical particle was observed at the bottom of each whisker.

The SEM images of sample B and sample D prepared at 1400 °C shown in Figure 5 and Figure 6.

![Figure 5. SEM images of and sample B at 1400 °C.](image)

Figure 5 showed the micrograph images of sample B cured at 1400 °C. The SEM images of sample B obtained at 1400 °C for 180 min without using Cu catalyst showing that silicon powder exhibits spherical particle or lamellar structure in phenolic resin, silicon powder is relatively uniform without obvious agglomeration such as(a). The surface of silicon powder is coated with a layer of sodium oxide, Sodium oxide comes from phenolic resin itself. The possible reason is that sodium vapor spills from phenolic resin during heat treatment and solidifies with the decrease of temperature, but the metal itself has poor wettability with C. Sodium vapor chooses to solidify on the surface of silicon powder, which leads to the phenomenon of sodium-coated silicon. At 1400 heat treatment temperature, a small amount of SiC columnar whiskers have appeared on the surface of silicon powder, means that the reaction had occurred but was still far from completion.

Figure 6 shows the micrograph images of sample D cured at 1400 °C. The SEM images of sample D obtained at 1400 °C for 180 min with using Cu catalyst which different from sample B with only silicon powder, showing that SiC whiskers could be observed at 1400 °C by using copper nitrate catalyst precursor. However, unlike SiC whiskers shown in Figure 5, Most of the SiC whiskers in Figure 6 could be divided into two morphologies in the sample containing 1.0 wt% Cu catalyst, one of which were about 5–20 μm in length and tens of nanoscale in diameter, the other were about 1–5 μm in length and hundreds of nanoscale in diameter. The results presented and discussed above suggested that Cu catalyst had played significant roles in accelerating the conversion from Si to SiC.
3.4. Thermal analysis results

Due to higher oxidation resistance in crystalline carbon phases compared to their amorphous state, by studying the thermal behavior of phenolic resins pyrolyzed at different temperatures, oxidation resistance of carbon derived from pyrolysis of Phenolic resin can be characterized by TG-DSC. TG-DSC spectra of sample A, B, C and D prepared at air atmosphere showed in Figure 7.

![Figure 6. SEM images of sample D at 1400°C.](image)

![Figure 7. TG-DSC spectra of sample A, B, C and D at air atmosphere](image)
The reactivity of the carbon sources varied as graphite is crystalline, while glassy carbon is amorphous. The differences in sample A to D reactivity were confirmed by their DSC and TG measurements.

An exothermic peak detected in the DSC curve of every treated sample. For sample A the exothermic peak appeared around 557°C; for sample C the exothermic peak appeared around 513°C; For sample B the exothermic peak appeared around 590°C; for sample D the exothermic peak appeared around 557°C; The exothermic peak of phenolic resin is higher than the temperatures at which the peaks of sample B appeared, means that the addition of silicon powder can fills the the pore and defect which produced by phenolic resin-pyrolysed carbon then reduces the contact area between carbon to oxygen.

TG curves shows that sample A and sample C he at-treated at 1000°C, thermogravimetric loss of the two samples after heat treatment at air atmosphere is large, and thermogravimetric of pure resin was almost complete means that the pure resin decomposes completely at 1000°C in airatmosphere. The thermogravimetric loss of resin sample C added with copper nitrate catalyst precursor was also larger, but it increased by 7.9% compared with that of pure resin., the ultimate char yield was up to 8.7% at 1000°C under air atmosphere. At the same times, TG curves results shows that sample B and sample D heat treated at 1000°C, thermogravimetric loss of the two samples after heat treatment at air atmosphere is lot less. Because silicon powder is added to sample B and sample D, and silicon powder will not lose weight at 1000°C, the overall thermogravimetric loss has some improvement compared with sample A and sample C. But sample B and sample D have the same rule as sample A and C. The thermogravimetric loss of sample D after adding copper and silicon powder is 7.9% less than that of sample B with only silicon powder. The results show that the addition of copper catalyst can catalyze graphitization of phenolic resin matrix to form carbon structure with higher degree of graphitization, the oxidation resistance of carbon nanofibers with high graphitization degree is stronger than that of glass carbon. It means that, with the addition of Cu to the phenolic resin, the oxidation resistance increased, due to the graphitization of the amorphous carbon obtained from the pyrolysis of phenolic resins with an Cu catalyst and the formation of graphic carbon nanofibers with higher oxidation resistance compared with amorphous carbon.

3.5. Phase composition
The Predominance area diagram for the Si-O-C-N system at 1000°C, 1200°C, 1400°C showed in Figure 8.

The Predominance area diagram for the Si-O-C-N system at 1000 °C, 1200 °C and 1400 °C in reduction atmosphere (coke bed) was calculated by thermodynamic FactSage software. Gases in buried carbon atmosphere consist of 65 % N2 and 35 % CO in volume fraction. Calculated according to the partial pressure of gas in the system $\lg[p(CO)]=4.944 \text{ Pa}$, $\lg[p(N2)]=4.813 \text{ Pa}$. Suppose the partial pressure of P(N2) is 65000 Pa, Si3N4 cannot be generated in this temperature range and the phase diagrams at different temperatures were obtained. The phase diagrams at different temperatures show that with the increase of heat treatment temperature, The requirement of oxygen partial pressure for SiC formation condition will be reduced. The addition of copper catalyst may further reduce the partial pressure of oxygen in the system, thus promoting the formation of silicon carbide whiskers.

4. Conclusions
Copper oxide decomposed by copper nitrate be reduced to elemental copper by reducing atmosphere. The copper nano-particles in-situ formed from copper nitrate can be served as catalyst in the pyrolysis process of resin. Catalytic synthesis of carbon nanofibers can improve the carbide with pyrolysis carbon microstructure at 600 °C. With the addition of Cu to the phenolic resin, the oxidation resistance increased, due to the graphitization of the amorphous carbon obtained from the pyrolysis of phenolic resins and the formation of graphic carbon nanofibers with higher oxidation resistance compared with amorphous carbon. Addition of Cu catalyst could promote the synthesis progress of SiC at 1400 °C.
Figure 8. Predominance area diagram for the Si-O-C-N system at 1000 °C, 1200 °C, 1400 °C
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