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# Formation mechanism of diamond nanocrystal from catalysed carbon black

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## Abstract

Recently, our group has synthesized nanocrystal n-diamond and diamond-like carbon (DLC) from catalysed carbon black. Based on the results of XRD, TGA and DTA, a formation mechanism has been proposed to explain the phase transformation from carbon black to diamond nanocrystal. With the increase of temperature and hence the carbon diffusion in iron, the phase sequence is from Fe(OH)<sub>3</sub> into Fe<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Fe,  $\gamma$ -Fe, then liquid iron. When the carbon in the liquid iron is saturated, DLC or graphite separates out of the liquid iron. With decrease of temperature, the carbon in  $\gamma$ -Fe is separated out, and n-diamond nuclei form and grow.

## 1. Introduction

Carbon materials have particular characters due to the differences in chemical bond formation [1]. Carbon forms three well-known allotropes that are distinguished by the type of electron hybridization: diamond, graphite and carbyne, with sp<sup>3</sup>-, sp<sup>2</sup>- and sp<sup>1</sup>-hybridization of the carbon atoms, respectively. All other known carbon modification, such as fullerenes, glassy carbon, and diamond-like carbon, are based on a combination of these three types of electron hybridization [2]. In the last ten years, a new kind of carbon allotrope was validated by Konyashin, Jarkov and their co-workers, which was a metallic form of carbon with face-centred cubic structure [2, 3]; in the literature, this phase was referred to as 'n-diamond'.

The n-diamond phase can be synthesized by various processes, such as radio frequency plasma-aided decomposition of hydrocarbon [4], plasma-assisted chemical vapour deposition

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using diluted hydrocarbons [5], transformation of graphite under shock-compression [6], transformation of C<sub>60</sub> films under shock-compression [7], transformation of graphite at high pressure and temperature [8], plasma-chemical synthesis with the aid of a carbon plasma jet [3], treatment of a diamond surface in hydrogen plasma [2], and annealing of a silica wafer embedded by carbon atom [9, 10].

In our previous works, we discovered that n-diamond and diamond-like carbon (DLC) could also be synthesized from catalysed carbon black at atmospheric pressure and at a temperature of 1100 °C [11]. In this paper the mechanism of phase transformation from carbon black to diamond nanocrystal will be discussed.

## 2. Experiment

An admixture of carbon black N231 powders (carbon black is an important technological raw material, which is produced by the thermal decomposition upon combustion of liquid and gaseous hydrocarbons in a deficit of oxygen at temperatures of ~1500 °C) and colloidal Fe(OH)<sub>3</sub> (from the reaction between FeCl<sub>3</sub> solution and NaOH solution) was compressed into an open stainless steel tank of 100 ml capacity. The mass ratio of carbon and iron in the mixture is 10:1. The tank was maintained at a given temperature for 10 min, and then cooled to room temperature; the heating rate and cooling rate were 10 and -30 °C min<sup>-1</sup> respectively. Finally, the phase composition of the heat-treated reactant was analysed by x-ray diffraction (XRD). Moreover, the thermal diversification of the admixture of the carbon black N231 powders and colloidal Fe(OH)<sub>3</sub> was investigated by thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) from 50 to 1580 °C, for which the heating rate was 10 °C min<sup>-1</sup> in flowing nitrogen.

## 3. Results and discussion

The XRD patterns were recorded on an XRD-6000 diffractometer with Cu K $\alpha$  radiation (wavelength 0.154 nm). Figure 1 shows the XRD patterns of the final powder that had been heat-treated at different temperatures (200, 400, . . . , 1600 °C). As shown in figure 1, when the treatment temperature was below 400 °C, only NaCl, the remnant of the reaction FeCl<sub>3</sub> + NaOH, was detected by the x-ray diffractometer. When the temperature reached 600 °C, Fe<sub>2</sub>O<sub>3</sub> was detected, and this was the result of pyrogenation of colloid Fe(OH)<sub>3</sub>. When the treatment temperature was 800 °C, the Fe<sub>2</sub>O<sub>3</sub> disappeared in the final reaction products, and the XRD patterns pointed to the presence of  $\alpha$ -Fe, n-diamond, amorphous carbon and NaCl in the final reaction products. The above results indicated that the  $\alpha$ -Fe was the product of the deoxidization-reaction of Fe<sub>2</sub>O<sub>3</sub> + C. In our previous work [11], the presence of n-diamond in the final reaction products has been described in detail, and the electron diffraction pattern and Raman spectrum verified that the amorphous carbon was DLC. With increased treatment temperatures, the peaks of n-diamond increase in intensity. When the treatment temperature reached 1400 °C, the intensity of the peaks of n-diamond achieved their maximal value. When the treatment temperature was above 1000 °C, the presence of graphite in the final reaction products was proved by the XRD patterns. In addition the background of the XRD patterns was enhanced with the increase of the treatment temperature, and this indicated that the yield of DLC increased. When the treatment temperature was above 1200 °C, there was no presence of NaCl in the final reaction products; this was the result of evaporation of NaCl.

Based on the XRD results, a formation mechanism of n-diamond nanocrystal from catalysed carbon black is proposed, and a phase transformation route is shown in figure 2.

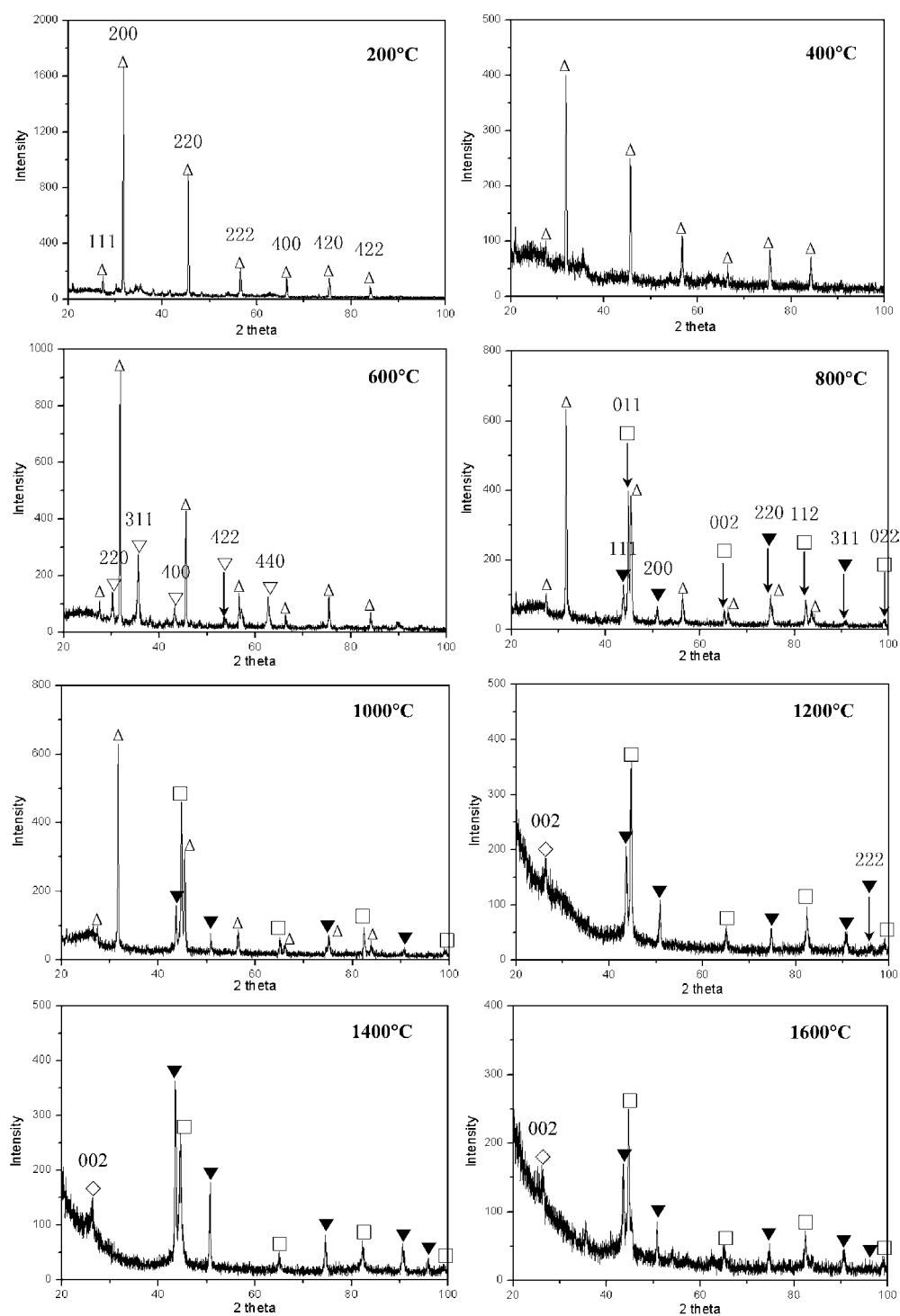
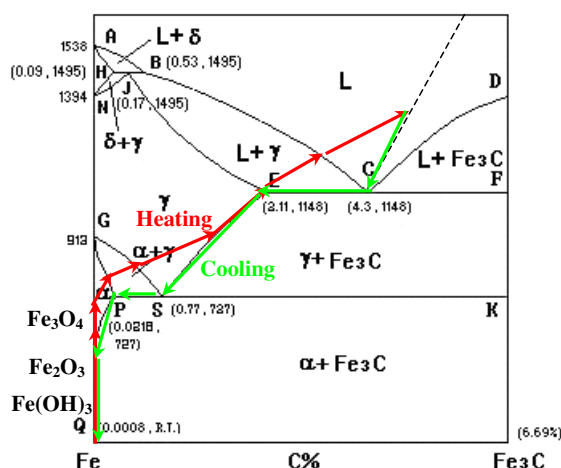
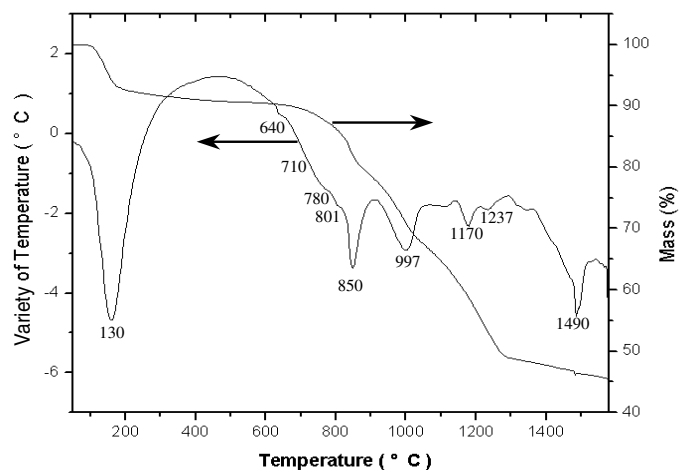


Figure 1. X-ray diffraction pattern of sample heat treatment at various temperatures. ▼ n-diamond, ◇ graphite, □  $\alpha$ -Fe,  $\Delta$  NaCl,  $\nabla$   $\text{Fe}_2\text{O}_3$ .



**Figure 2.** Routes of phase transformation.  
(This figure is in colour only in the electronic version)



**Figure 3.** TGA and DTA curves of the admixture.

With increase of temperature and carbon diffusion in iron, phases formed from Fe transformed from  $\text{Fe}(\text{OH})_3$  into  $\text{Fe}_2\text{O}_3$ ,  $\alpha$ -Fe,  $\gamma$ -Fe, then liquid iron (L). When the carbon in the liquid iron was saturated, DLC or graphite was separated out of liquid iron at high temperature [12–14]. Since the lattice structure of  $\gamma$ -Fe is the same as that of n-diamond,  $\gamma$ -Fe can be the nuclear point of the n-diamond. With decrease of temperature, the carbon in  $\gamma$ -Fe was separated out, and n-diamond nuclei were formed and grew. The DTA results validated this.

Thermal analysis was done for the admixture of the carbon black N231 powders and colloidal  $\text{Fe}(\text{OH})_3$ . Figure 3 shows the DTA and TGA curves of the admixture; the intensity endothermic peak at 130 °C was associated with the decomposition of colloidal  $\text{Fe}(\text{OH})_3$ . The broad exothermic peak (from 130 to 710 °C) is the deoxidization-reaction  $\text{Fe}_2\text{O}_3 + \text{C} \rightarrow \alpha\text{-Fe}$  and the weak peak at 640 °C indicates the transformation from  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$ ; the peak at 710 °C is the end of the reaction  $\text{Fe}_3\text{O}_4 + \text{C} \rightarrow \alpha\text{-Fe}$  [15]. The peaks at 780 and 801 °C show

the beginning of the reaction  $\alpha\text{-Fe} \rightarrow \gamma\text{-Fe}$  and the melting point of NaCl respectively, and the intensity peaks at 850 and 997 °C correspond to the beginning and the end of the reaction  $\alpha\text{-Fe} \rightarrow \gamma\text{-Fe}$ , respectively. The peak at 1170 °C is the beginning of the reaction  $\gamma\text{-Fe} \rightarrow \text{L}$ , and that the peak at 1237 °C is the end of the reaction  $\gamma\text{-Fe} \rightarrow \text{L}$ . The intensity endothermic peak at 1490 °C is the reaction of carbon black + L  $\rightarrow$  DLC + graphite + L. The DTA curve corresponds to the TGA, i.e. the deoxidization-reaction  $\text{Fe}_3\text{O}_4 + \text{C} \rightarrow \alpha\text{-Fe} + \text{CO}_2$  peak (from 640 to 710 °C) was just in the range of the significant weight loss.

#### 4. Conclusions

Based on the results of XRD, TGA and DTA, a mechanism has been proposed to explain the phase transformation from carbon black to diamond nanocrystal. With increase of temperature and carbon diffusion, phases form from Fe-atoms transformed from  $\text{Fe}(\text{OH})_3$  into  $\text{Fe}_2\text{O}_3$ ,  $\alpha\text{-Fe}$ ,  $\gamma\text{-Fe}$ , then liquid iron. When the carbon in the liquid iron is saturated, DLC or graphite separates out of the liquid iron at high temperature. With decrease of temperature, the carbon in  $\gamma\text{-Fe}$  is separated out, and n-diamond nuclei form and grow.

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